ON MAGNETIC ROTATORY POWER, ESPECIALLY OF AROMATIC COMPOUNDS.

BY

W. H. PERKIN, LL.D., PH.D., F.R.S.

[From the Transactions of the Chemical Society, 1896.]

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SECTION I.—INTRODUCTION.

THE original object of this communication was the study of the magnetic rotation of substances belonging to the aromatic series, and was intended as a sequence to that on the fatty compounds presented to the Society in 1884; the work, in fact, having been in progress ever since the completion of that paper, now more than 11 years.

The results obtained in the examination of compounds of the aromatic series gradually accumulated, and it was in contemplation to bring them before the Society from time to time. On carefully comparing the rotation of these compounds, however, it was found that there were anomalies which made it undesirable to publish the work until more complete data had been collected by the measurement of a larger number of substances allied to one another. Moreover, it was found that some of the peculiarities of aromatic compounds also occurred in the fatty series, although, as they were less marked they had not previously been fully recognised. It was ultimately decided, therefore, that it would be better to wait until the various points which presented themselves at different times had been, to some extent, studied, and then not to confine the paper to the discussion of the rotations of aromatic compounds only, but to include other information in reference to magnetic rotations which had been acquired since the communication published in 1884.

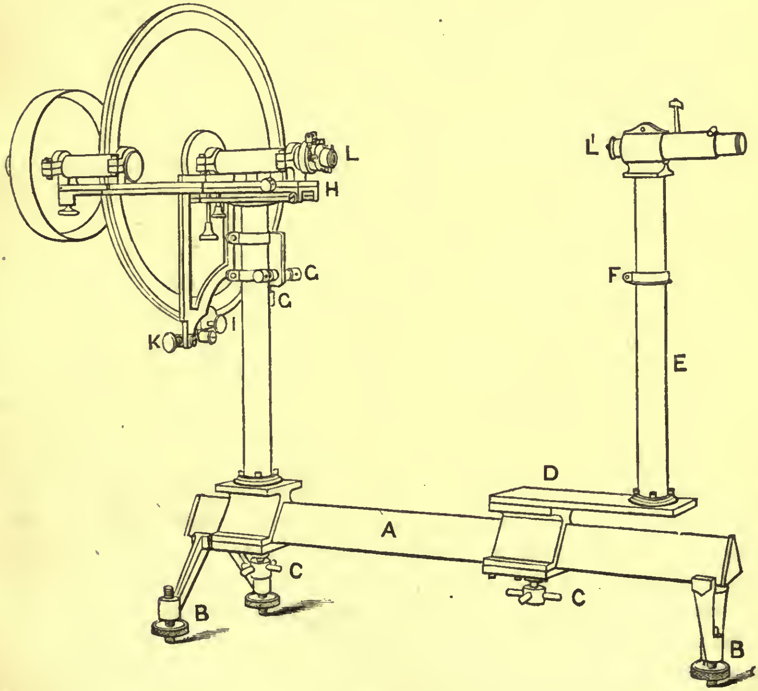
Although the following account of the work done and the results obtained is still not so complete as could be wished, it is, at all events, likely to be useful, and to indicate fresh starting points for future investigation.

Apparatus.

The apparatus used in the following determinations is of the same form as that described in 1884, the substance to be examined by polarised light being contained in a tube with parallel glass ends placed in the magnetic field between the two pierced pole pieces of a large electromagnet.

The electromagnet is the same as that described in the paper just referred to, but the optical arrangements are all new, and represented in Figs. 1 and 2.* In the old apparatus, the polariser and analyser were on two separate supports, and as this arrangement was imperfect on account of the danger there was of shifting taking place, it was thought best to have these two parts of the apparatus firmly connected. This is accomplished by placing them on two pillars which slide on an accurately planed triangular bar, or bed, 76 cm.

FIG. 1.



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* This apparatus was made by Hilger.

(2 ft. 9 in.) long, A, Fig. 1, supported on strong feet, provided with levelling screws, B, B; they can thus be shifted backwards or forwards as may be required, and then securely clamped by the screws, C, C. The foot of the column supporting the polariser is connected with a strong horizontal piece of brass, D, which connects it with the clamping arrangement, in case it might be found desirable to place the polariser at a greater distance from the analyser than the triangular bar would permit, as, for instance, if the apparatus had to be used in connection with a coil; by this means, the distance between the polariser and analyser can be extended to about 61 cm., or 2 ft.

The polariser can be raised or lowered, as it is fixed on a tube sliding within the column E; this also allows of its being moved on its centre. It is fixed in its place by means of the screw F.

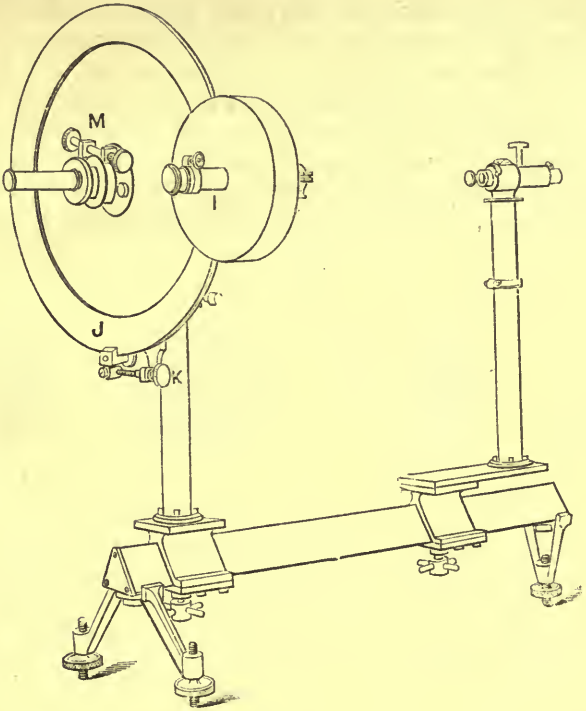
The analyser can also be raised or lowered, or turned on its centre in the same manner as the polariser, but it is, moreover, provided with special screws G, G, so that these adjustments may be made very accurately, and then the position firmly fixed. The head of this sliding tube, which carries the divided circle as well as the analysing prism, is so constructed that it can be moved to some extent in any direction, and then fixed firmly by screws. These arrangements are seen at H. No iron was used in the construction of this apparatus, though probably this is not a very important point.

The circle is 40·5 cm. (16 in.) in diameter, and is provided with an edge made of white metal (platinite) on which the divisions are marked. The divisions are the 1/12th of a degree; this scale gives, with a vernier of a comb shape, which is placed in the eye-piece of the highly magnifying telescope I, Fig. 2, the 1/120th of a degree, or 30 seconds of arc. The scale is reflected into the telescope by means of a right angled prism, and illuminated by means of a small gas jet in a brass lantern. As all the determinations I have hitherto made have been relative to the rotations of water, and only a small part of the circle has, therefore, been used, a double vernier has not been required. It has also been found experimentally that the relative rotations measured with the polarising prism and circle at the two positions 180° apart give practically the same results. J is a clamp to fix the circle when roughly adjusted by hand, and K is a double threaded screw for the fine adjustment. At first, a single threaded screw was employed, but it was found to give too slow a motion for the eye to readily discern the changes in the shadow.

The position of the analysing prism is adjusted by the tangent screw M, Fig. 2.

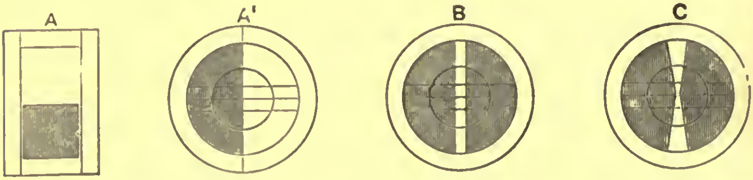
In my original apparatus, the arrangement for producing the half shadow was next to the polariser, but it was found that when working with substances liable to form convection currents a great deal of time was wasted in waiting until these disappeared and a good image was obtained, notwithstanding the temperature was practically constant; it was, therefore, decided to have it placed next to the analyser, so that any slight convection currents would not affect the image; this has been found a great advantage, especially when the substances under examination are heated nearly to the temperature of boiling water, as it is then less easy to maintain a perfectly constant temperature for a considerable time than under ordinary circumstances, moreover, it is undesirable, in many cases, to keep substances heated for a long time before measurement, as they are liable to become coloured, or other changes may take place. Of course it is not advisable, if it can be avoided, to take readings when much convection is occurring; provision was also made so that the half shadow arrangement could be used next to the polariser if desired.

Fig. 2.



Instead of using the ordinary half quartz plate, the arrangement described by Professor Poynting (*Proc. Phys. Soc.*, 1881, **4**, 19) has been employed, consisting of a glass cell, part of which is occupied with a piece of glass, and the rest with a strong solution of sugar, as it was thought to give a more uniform field. The cell used, which was circular, as it had to revolve with the analyser, was made of a piece of glass tubing 9 mm. long, having the ends covered with two discs of parallel glass. The glass which is introduced into this cell is only about 7 mm. thick, so that the sugar solution passes over its two side surfaces, and in this way a fine dividing line is obtained, provided the optical adjustments are good. A section of this cell is seen in Fig. 3, A. The piece of glass occupying the half of the cell should be perfectly homogeneous, otherwise striæ will be seen with polarised light; plate glass, however, may be used, provided its ordinary surface be opposite the eye, and not the edge. This piece of glass has to be very carefully prepared, as the edges must be perfectly sharp and free from any roughness; it is fixed in position in the cell with Canada balsam. The sugar solution used contained 50 per cent. of sugar; when filling the cell, care must be taken to remove any small air bubbles from the surface of the glass, as these often adhere to it, but a movable larger one is not of importance, and is sure to form after a time. Lippich, who produces the shadow by means of a polarising prism, has, of late, found it advantageous to use two prisms, so as to give two shadows, one on each side of the field; I have copied this by having two pieces of glass in the sugar cell instead of one, B, Fig. 3, and this appears to be an advantage. An analogous effect may be obtained by simply using a narrow piece of glass across the centre; in Fig. 3, A′, B, C represent the front views of the different arrangements used. The small circle in the centre of each shows the size of the field employed in relation to the size of the cell. The cross lines dividing the field into bands are to assist the eye in making the measurements always on the same part of the cell, because, as in all other arrangements of a similar nature experimented with, the field is not perfectly uniform (see Trans., 1884, **45**, 435). Of these cells, the one marked C seems to be the most pleasant to work with, the only disadvantage being that when an air bubble forms it is liable to rise up between the two pieces of glass and remain wedged in the narrowest part; this, however, only occurs if the circle is reversed, and even then there is plenty of field free for

FIG. 3.



reading. By having the two sides of the field of a uniform character, as happens when employing the cell arranged as in B or C, the eye is prevented from resting too much on one or other of its sides, as occurs in the half shadow form, especially if there is a slight difference in their colour. It seems likely that instead of using two polarising prisms, as in Lippich's arrangement, a thin one placed across the centre of the field might be employed. This arrangement is being tried.

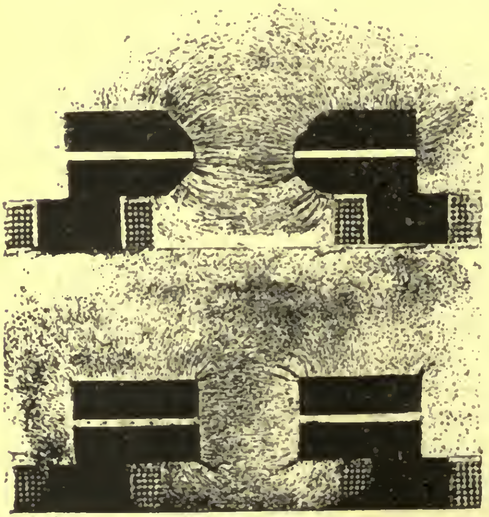
The glass sugar cells are fitted into small holders at L and L′, Fig. 1.

The monochromatic light employed has been produced by the method previously described, namely, burning a mixture of hydrogen and sodium vapour, and is then purified by passing it first through a solution of copper sulphate and afterwards through a dilute solution of eosin; the latter is preferable to potassium dichromate solution, as it cuts off the green rays better. This light can be intensified very considerably by causing oxygen to impinge on the flame, and this is sometimes a useful artifice to adopt when the substance under examination is coloured slightly brown or orange; in fact, in all cases where it is difficult to get sufficient light to pass through the substance when using the ordinary monochromatic light. When using oxygen, it is necessary to make sure that the liquid is well screened from the more refrangible rays the light then contains, although if the substance to be examined is of an orange or brownish tint, there is no danger of this; in fact, if it is so deep coloured as to make it very difficult to take readings, it is an advantage to remove the eosin screen and rely on the colour of the liquid to act in its stead.

If the rotation of the substances is large, this sodium light is found not to be so thoroughly monochromatic as could be wished, even when the amount of eosin and copper sulphate solution is largely increased; this is probably rendered more apparent than usual, owing to the low angle of the shadow arrangement I prefer to work with. No doubt it would be a great advantage to purify the light with a prism if sufficient intensity could be obtained. I have not used the light advocated by Messrs. Rodger and Watson with my apparatus as yet, but the drawback to it is that it is apparently a costly light, not only on account of the amount of hydrogen it consumes, but because the spray used can only be obtained while the pressure of the gas is very high; on this account only about half of the gas in the cylinder can be used for the production of this light. When the light is not perfectly monochromatic, more judgment has to be exercised in the observations than when it is pure, for it then becomes a matter of judging of the similarity of intensity of shades differing slightly in colour, although by repeating the measurements on different occasions, any error due to this source is, no doubt, eliminated.

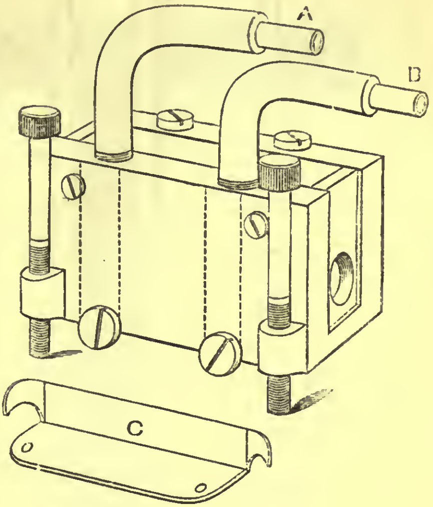
In my previous paper it was mentioned that each of the pole pieces was made conical at one end because it was expected that by using them with these ends opposed to each other, a more concentrated field would be obtained, and measurements would be larger; on trying this experimentally, however, it was found that the readings were actually smaller than when the square ends were opposed to each other (Trans., 1884, **45**, 430). As some doubt seemed to arise as to the cause of this, I had the curiosity to examine, by means of iron filings, the direction the lines of force took under both circumstances. To do this, pieces of cardboard, thoroughly saturated with paraffin, were fitted centrally between and partially around the pole pieces; and after being dusted with iron filings the battery was connected with the electromagnet, and the cardboard warmed by a spirit lamp until the paraffin had melted; it was then allowed to cool, and when the filings had become firmly fixed the battery was disconnected. The diagrams thus obtained are represented in Fig. 4, taken from a photograph. It will be seen from these that the lines of force from the conical ends are nearly all curved, whilst those from the square ends are all straight, or nearly so, in the central part of the field, becoming a little curved near the outside edges of the pole pieces. This clearly shows why the flat ends were found experimentally to form the best field.

FIG. 4.



In the old apparatus, the measuring tube containing the substance under examination was supported on a little wooden carriage passing between the pole pieces, and no means existed for regulating the temperature other than that of the atmosphere of the room, which was more or less fluctuating. A thick cast copper cell, Fig. 5, is now used, 204 mm. long, and thus just the size to pass between the pole pieces, usually placed 205 mm. apart. In the walls and bottom of this cell, which are about 15 mm. thick, holes about 7 mm. ($\frac{1}{4}$ of an inch full) were drilled, and so arranged that water can circulate through them, passing in at A, and flowing out at B. The two ends of the cell are also of copper about 4 mm. thick, and provided with circular apertures a little larger than the diameter of the measuring tubes, so that the latter may easily be placed in the cell with their two ends slightly projecting through these holes. This cell is provided with levelling screws, by means of which the position of the measuring tubes can be easily adjusted in relation to the perforations in the pole pieces.

Fig. 5.



Trouble used to be experienced by the two iron cylinders of the electromagnet becoming heated by the current, and by conduction raising the temperature of the pole pieces, and these again influencing the temperature of the substance in the measuring tube; and although this inconvenience was obviated to some extent by placing on the pole pieces copper vessels through which water circulated, the result was not very satisfactory. Channels similar to those in the copper cell just described were, therefore, also drilled in the pole pieces, and water made to circulate through them; this, however, was not quite sufficient, and eventually channels were also drilled in the cylinders of the magnet itself, and thus by passing a current of water through the copper cell, the pole pieces, and then through the cylinders of the magnet, a uniform temperature could be maintained. This arrangement of channels or water-ways is shown in Fig. 6, which gives a section of the electromagnet showing these, and Fig. 7, which gives a perpendicular section of the pole pieces and cell, the latter with its three sides, A, B, C, laid out to more clearly show the course of the channels.

Originally, when determining rotations a little above the atmospheric temperature, the atmosphere of the room used to be heated

FIG. 6.

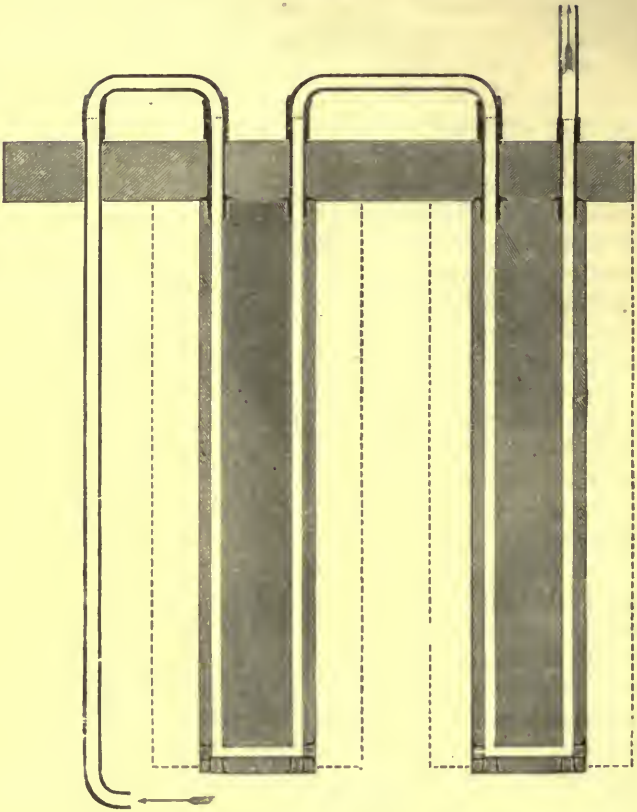
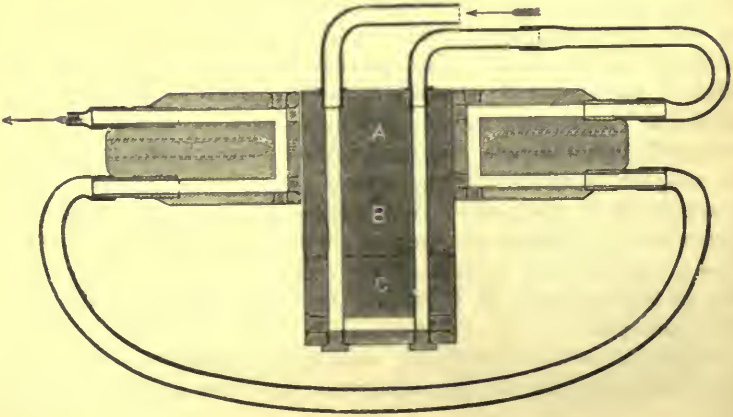


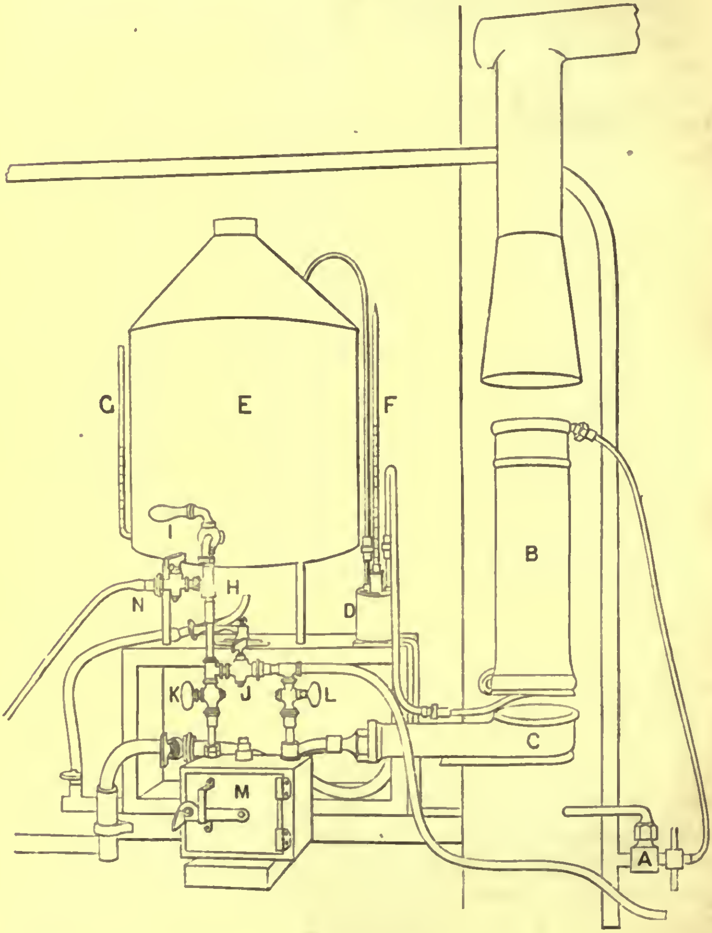
FIG. 7.



by means of a gas stove; this, however, was not only a slow and troublesome method, but it did not allow of large variations of temperature being employed; moreover, when studying the aromatic compounds, it was found necessary, in many cases, to employ temperatures nearly up to the boiling point of water in order to get the desired comparisons, because certain sets of substances such as ortho-, meta-, and para-derivatives, could not otherwise all be obtained in the liquid state. This is especially the case with para-compounds, which are so frequently solid at the ordinary temperature, and therefore have to be fused in order to examine them; moreover, for the purposes of investigating these substances it was absolutely necessary to be able to make measurements at temperatures wide apart. With the system of channels above described, this could be accomplished by allowing water of different temperatures to circulate through them; as the specific heat of water is so much greater than that of metals, the amount of water passing through the channels is sufficient to raise and maintain the cell and pole pieces nearly at 100° when boiling water is used, and, consequently, also to heat the iron cylinders sufficiently to prevent them from absorbing any large amount of heat from the pole pieces. A few additional degrees of heat may also be obtained by allowing the flame of a Bunsen burner to play on the side of the copper cell whilst the boiling water is circulating; in this case a small copper shield, C, Fig. 5, is screwed on the front of the cell to prevent the flame from burning the vulcanised tubing with which the copper tubes conveying the hot water are covered to avoid loss of heat by radiation. It may here be mentioned that all the water tubes connecting the water channels were covered in this manner.

To maintain the apparatus at a practically even temperature, it is obviously necessary that the temperature of the water circulating through the channels should also be kept constant, and a good supply provided; for this to be continuous it must be heated as it flows from the main or tank. For this purpose a regulating valve is required, such that when once regulated, the amount of water passing will not vary. In constructing it, all leather or elastic seatings must be avoided, and the valve surfaces be metal to metal, because, compressible substances do not regain their original condition at once, when the pressure is removed, and, therefore, if used for a valve of this kind, would not give a regular delivery of water. A valve similar to that used on compressed gas cylinders, but rather larger, has been found to answer the purpose very well. The gas supply for heating the water must also pass through a regulator. The arrangement for the supply of water at different temperatures is represented in Fig. 8; A, is the water valve, from which the water passes through one of Fletcher's water heaters, consisting of a coil of small copper tubing, B, heated by a powerful air gas burner, C; from the heater, the water passes into the small three-necked copper vessel D, and thence into the large copper reservoir E. When passing through the small three-necked vessel, the

FIG. 8.



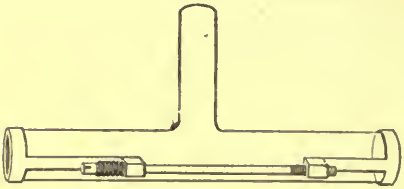
temperature of the supply is indicated by the thermometer F, and that in the large one by the thermometer G; this large reservoir is well covered with flannel, and a small burner, H, is also placed under it to keep it up to boiling when such a high temperature is required.

When preparing the apparatus for use at temperatures above the ordinary, say at about 50°, and assuming the reservoir to be partially filled with cold water, water near the boiling point is passed into it from the copper coil until the thermometer G indicates about 50°; the gas is then turned down until the thermometer F, in the three-necked vessel also indicates 50°, when the supply after a little more adjustment can be kept sufficiently regular for measurements to be made. When using high temperatures, the water is usually allowed to pass directly to the copper cell, &c., from the stopcocks I and J, but when temperatures about 30° or below are employed, the stopcock, J, is closed, and K and L opened; by doing this, the water circulates through a small water oven, M, before it passes on to the copper cell, &c. The object of this water oven is, that tubes filled with the substances to be examined, may be placed in it, so that when they are required, they may be of the same temperature as the copper cell into which they are to be transferred for examination; time is thus economised. This apparatus for supplying water at different temperatures is also employed in connection with the arrangements used for refraction determinations, the water being supplied from the stopcock N.

The tubes in which the measurements are made are of the same kind as those previously described, a considerable number being employed; their ends are very carefully ground perfectly parallel to each other, and they are also made of exactly the same length. Instead of closing the ends with thin microscope glass, as formerly, discs made of plane parallel glass about 1·23 mm. in thickness are used. These were all cut out of one piece of glass, so that their thickness might be exactly the same, and their influence on the rotation measurements identical; by using these ends, a better optical field is obtained than when microscope glass is employed. These ends are fastened to the measuring tubes by means of a preparation of glue for oily liquids, and with amber or other oil varnish and red lead well ground together, for aqueous solutions; tubes with ends cemented on with the latter mixture should be kept a week or longer before being used. Silicate of soda has been proposed as a cement; but as both the tubes and ends are valuable, and require to be often separated to be thoroughly cleaned and the ends rendered bright, it is not suitable for the kind of measuring tubes described above.

When employing temperatures approaching that of boiling water, the glue cement is liable to become brittle, and that made with varnish soft, especially if recently used, and the glasses therefore are liable to come off if at all roughly handled; this is, of course, serious when the tubes are filled with valuable materials. To protect the ends, and also to prevent them coming off under such circumstances, an arrangement shown in Fig. 9 is employed. It consists of two thin brass caps which fit over the ends of the measuring tube, and are perforated so as not to interfere with the light which has to pass through the tube; these are held together by means of two small screw rods, springs being placed behind the heads of the screws so as to neutralise the effect of the expansion of the metal by heat; by using this arrangement, it has been found that the glass ends very rarely come off or leak.

FIG. 9.



Before making measurements, the corrections for the glass ends of the tubes, and for the effect of the magnetic radiation on the optical parts, have to be determined; these corrections are treated as one, and can be determined together. That for the glass ends is a + quantity, and that for the optical parts a − quantity, so that these neutralise each other to a great extent, and only change when any alteration is made in the position of the polarising prisms or other optical parts. In order to determine this double correction, all that is necessary is to place an empty tube in the copper cell and ascertain the rotation when the current is used in opposite directions; in my experiments this has varied from about −2′ to −4′. Being a minus quantity, it has to be added to each rotation determination, but, of course, if changes in the arrangement be made so that it becomes a + quantity, it would have to be subtracted from each rotation.

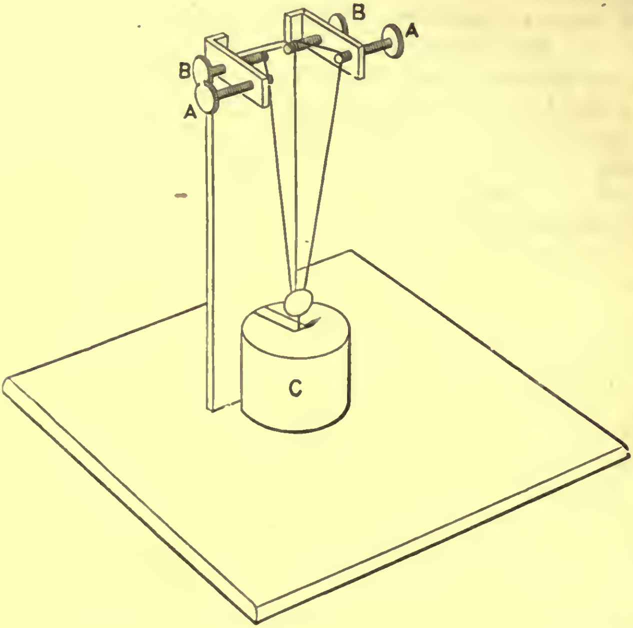
Hitherto, before commencing work, I have almost invariably determined the above correction, and also standardised the apparatus by measuring the rotation of water, lest any shifting of the pole pieces or other changes should have taken place since the apparatus was last used; this was useful, because any errors made on one occasion would be corrected on the next and not repeated. By using a battery power of 22 ampères, the double rotation of water amounts to about 5° 40′. For standardising purposes, water possesses several advantages, notwithstanding that its rotation is not large its expansion is very small, especially at ordinary temperatures; it can always be obtained of the same purity; it does not show convection currents with slight changes of temperature; and, lastly, it furnishes a very clear field in the polariscope. The advantage to be derived from the larger rotation of other substances which might be used as standards, is usually counterbalanced by some disadvantage.

Of late, fresh experiments have been made on the determination of rotations at temperatures above the ordinary by heating the copper-cell alone and keeping the pole pieces and magnet cold; this has been done by interposing a layer of non-conducting material between the pole pieces and copper cell, so as to stop the loss of heat due to conduction. The advantage of this is that time is saved, the cell being more quickly heated than the whole apparatus; on the other hand, owing to the thickness of the non-conducting material, the pole pieces are a little further apart, and this reduces the rotation slightly, although not seriously; moreover, if the non-conducting material is inefficient, the temperature of the substance near the ends of the tube is liable to be slightly different from what it is in the middle; so far, however, as experiments have been made, these possible sources of error do not appear to have any practical effects on the results.

The electric current has been derived, as in the earlier work, from Grove cells (Trans., 1884, **45**, 423), 28 of them, with platinum 20 × 10 cm., being used, arranged in two series coupled together. A constant current has also been employed, being maintained by the use of the arrangement with a varying resistance previously described (Trans., 1884, **45**, 441). This apparatus works very satisfactorily if the platinum wires and contacts are properly amalgamated with sodium amalgam each day before it is used. It has been found that the platinum wires do not become brittle by amalgamation, those now in use having been employed for about 11 years, and they are still in good condition.

The galvanometer used is influenced by the entire battery current. It consists of very thick copper wire making three turns of a circle about 50 cm. in diameter. The small magnet and mirror are suspended by two cocoon threads spread out so as to control the amount of the deflection. This arrangement is shown in Fig. 10, the four screws A, A, B, B being used for the adjustment of the suspending cocoon filaments; the latter are first attached to the two back screws, B, B, on which they can be wound so as to raise the mirror and magnet to the desired height, and they also pass over grooves at the ends of the two front screws, A, A, so that by turning these the threads may be drawn apart, or made to approach each other; in this way the swing can be adjusted according to the current used. The mirror is flat and illuminated with light from a slit by means of a convex lens, the image of the latter being thrown on a screen; this screen is 2 metres long, and the deflection produced by a variation of current producing an alteration of 1′ in the magnetic rotation of water is about 15 mm. The magnet is suspended from the mirror by a thin platinum wire, and hangs in the little cylindrical vessel, C, which is filled with bromonaphthalene; this acts as a paddle, and produces a very rapid dead heat. The vessel C is provided with a lid having a slit in it so that it may be easily placed in position after the magnet and mirror have been adjusted. The apparatus, protected from dust and draughts by means of a case provided with a glass front, is placed on a stand in the centre of the 50-cm. circle of copper wire.

Fig. 10.



Before leaving this subject of the apparatus used for the measurement of magnetic rotations, it is worth while to consider whether the above is the most suitable arrangement or whether it is better to employ a long coil of wire in place of the electro-magnet; no doubt, for some special purposes, the coil has certain advantages; for example, the apparatus used by Messrs. Rodger and Watson is specially useful for the determination of absolute values, because the value of the magnetic field is known; it is also particularly suitable for the very accurate measurement of temperature differences of some classes of substances; moreover, it gives large rotations with a comparatively small electric current. For general work, however, such as that connected with this paper, it has many drawbacks; first, the great length of the tube containing the substances to be measured, which in the apparatus just referred to is 62 cm., not only necessitates the use of a considerable amount of substance, but the latter must be absolutely bright and colourless, or of only a very pale and pure yellow colour, otherwise sufficient light will not pass to allow of readings being taken. It is remarkable what a very slight amount of colour, even with the short tubes employed in my apparatus (102 mm.), renders readings almost impossible; in fact, a substance which appears only very slightly coloured when in a bottle, appears very deep coloured when seen in a tube of the length just mentioned. The aromatic amines are in many cases difficult to obtain free from colour, and if heated for some time in the measuring tubes, as they are in the determination of temperature differences, they soon become coloured. Some phenols, and many other substances, especially nitro-compounds, it would be impossible to measure in a long tube, and it would also be a matter of great difficulty to determine the rotation of fused substances in the long tube necessitated by the coil arrangement, especially if the fusing point was at all high. This apparatus, moreover, appears to require a very intense light. For general work, therefore, the electro-magnet is more useful than the long coil, and the absolute measurements of water having been once accurately determined by means of the coil, it is easy to calculate that of all other substances which have been measured relatively to water.

With respect to absolute measurements, no doubt they are of great value to physicists, but, from a chemical point of view, it does not at present appear that they will be of any special importance, the interest connected with the magnetic rotation of substances being chiefly in their relationships to each other. Magnetic rotations of the elements, so far as can be gathered from the present data, do not appear to be related to their atomic weights, and, moreover, if it were so, very few of those which could be used as standards of comparison are capable of measurement in the free state. Water, on the other hand, which has the smallest molecular weight and molecular rotation of any liquid substance known, and can easily be obtained pure, appears to be the most suitable unit of reference, at any rate, in the present state of our knowledge.

It is of interest to notice that the measurements made with the coil and electromagnet agree very closely, showing that both forms of apparatus give the same results.

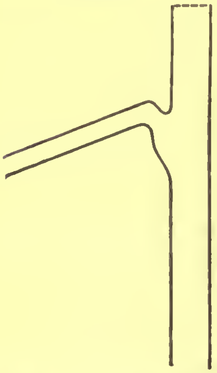
Boiling Points.

When taking the boiling points of compounds referred to in this paper, especially of those of the aromatic series, which are usually high and often very high, the entire column of the mercury has been exposed to the vapour, as is now so frequently the practice. In these determinations, the top of the column was kept a little below the delivery tube, so as to be thoroughly heated; this necessitates the use of a distilling flask with a rather long neck. This method has, in all cases been adopted, because the usual correction for that part of the mercury column which is not heated, as in the ordinary way of conducting distillations, was not thought to be sufficiently accurate, especially when the temperature is high; for, if the centre of the cork is taken as the point from which the outside column is measured, it assumes that the portion of the column below the cork is at the temperature of the vapour of the liquid, a condition which only exists when the distillation is carried on very rapidly, and this is usually very undesirable.

If the thermometer has a partial vacuum in it, the mercury in the column distils up into the capillary tube when it is heated above 200°; to avoid this, it is advisable to keep the thermometer drawn up, so that the column is just within the cork, and then to lower it for a few moments, now and then; and as soon as it has become well heated by the vapour to take the readings. It is, however, far preferable to use thermometers filled with nitrogen, as, in these, distillation of the mercury does not take place.

The liquid produced by the vapour which condenses on the cork becomes coloured at times, and, in the ordinary way of distilling, some of it passes into the delivery tube as it runs down, and stains the distillate. This is very undesirable in the case of liquids required for magnetic rotations, which must be as free from colour as possible. The delivery tubes of the distilling flasks now used are therefore arranged as in Fig. 11, so that none of the liquid which condenses in the neck can get into the delivery tube.

FIG. 11.



After taking the boiling point of substances, it has been my practice in most cases to immediately take that of some other well-known substance, boiling at nearly the same temperature, using the same thermometer under the same conditions. In this way the correction required for this standard substance, due to the barometric pressure and error of the thermometer employed, is found; this correction is then applied to the observed boiling point of the substance under examination. If the two substances vary much in boiling point, a further correction is made for this difference. The substances generally used for comparison were, water, 100°, aniline, 184°, naphthalene, 218°, and benzophenone, 306°.

At high temperatures, it cannot be expected that the boiling points will be comparable in accuracy with those obtainable for substances boiling at comparatively low temperatures, and, in fact, there is little doubt that the majority of aromatic compounds of high boiling point undergo decomposition to a small extent if kept in a state of ebullition for any great length of time; it is evident, therefore, that, in taking boiling points of substances like these, under the ordinary pressure, it is undesirable to be long over the operation or to use too much substance.

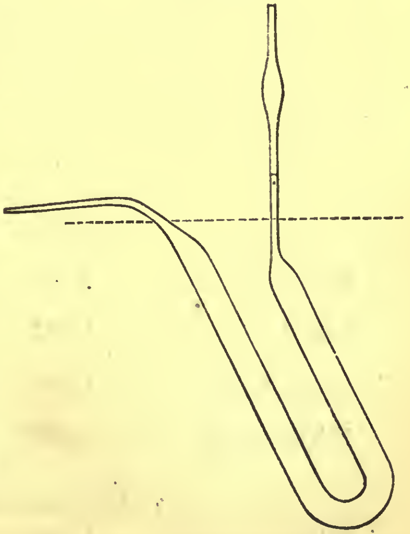
As all the boiling points given are comparable, it has been thought worth while to make a list of them, side by side with some of those given for the same substances in Beilstein's *Organische Chemie* (2nd and 3rd editions).

A considerable number of substances had their boiling points taken under reduced pressure, and in these cases also the whole mercury column was kept in the vapour.

Determinations of Densities.

For these determinations, the modified Sprengel tube, previously described, was used (Trans., 1884, 444), but slightly altered in shape, one arm of the U-tube being made a little shorter than the other, as seen in Fig. 12. The advantage of this is that when adjusting the level of the liquid, with which it is filled when in use, to the marked position on the capillary tube by tilting it, there is no fear of the top of the U-tube being brought above the surface of the water bath in which it is immersed. In making these tubes, it is desirable to use glass as thin as is consistent with rigidity, but it must not be so thin that any elasticity is shown in the U-tube under ordinary usage, because, if bent out of shape, its capacity will slightly alter.

Fig. 12.



The capacity of these tubes was usually determined with water at 4°, one advantage being that at this temperature the weight of water contained in a glass vessel varies very little on the plus side of this, even with a change of several degrees, being practically the same at 7·5° as it is at 4°, so that the weight of a tube of 10 c.c. capacity filled to the mark with water would not differ at any point between these two temperatures by more than about 0·00015 gram.

The density tubes generally used contained from about 7 to 10 c.c. It has been found quite indispensable to have a bulb on one of the capillaries of these tubes, but it may be objected that, should this bulb become moistened with the substance under examination, and if no precautions be taken to remove it before the final adjustment is made, a small error might be introduced. Experiments were therefore made in order to ascertain what the probable extent of this error would be; for this purpose, two bulbs, similar to those on the density tubes, were employed, one of which contained 0·48 c.c., which would be rather large for a tube holding 10 c.c.; the capacity of the other was 0·16 c.c. As the amount of liquid which would adhere to the walls of these bulbs would vary, of course, with its physical character, the effect of different kinds of liquids was tried. The liquids used were pseudocumene, ethylic phthalate, bromobenzene, and ethylic iodide; as is well known, ethylic phthalate is rather a thick fluid. The temperature was about 8°.

The weighed bulbs were in some cases filled with the liquid, and in others only half filled (in practice the latter is rather more than would be likely to flow into the bulb); they were then allowed to drain for definite lengths of time and reweighed, the difference of the two weighings giving the amount of substance remaining in the bulbs. Without giving all the details, the following table will furnish the results obtained for the bulbs when half their surfaces were wetted, and the influence the amount of liquids retained would have on the densities, assuming the tubes to contain 10 c.c.

1. *Bulb containing* 0·48 *c.c.*

Substance.	Density, 15°/15°.	Time of draining in minutes.	Effect on density.
Pseudocumene	0·8810	1	0·00006
		2	0·00004
Ethylic phthalate ..	1·1268	1	0·00034
		4	0·00015
Bromobenzene	1·4991	1	0·00007
		3	0·00004
Ethylic iodide	1·9492	1	0·00005
		3	0·00003

2. *Bulb containing* 0·16 *c.c.*

Ethylic phthalate ..	1·1268	3	0·00011
		1 hour	0·00007
Bromobenzene.....	1·4991	1 minute	0·00001

From these results, it is seen that the amount of liquid left on the walls of the bulbs which have been half filled and then allowed to drain for only one minute affects the density so little, except in the case of ethylic phthalate, that, for most purposes, the error may be ignored, whilst, even in the case of ethylic phthalate, it becomes very small if the draining is allowed to go on for three minutes. The small quantity on the walls of the bulbs can, however, be removed after the liquid in the density tube has been roughly adjusted, by heating it carefully; this causes most of it to run down, and volatilises the rest; after this the final adjustment can be made. I have not, however, usually done this except in the case of viscous liquids, but have always made it a practice to approximately adjust the liquid in the tubes after they have been in the water bath a few minutes, and then allow plenty of time for the bulbs to drain well before making the final adjustment. The results are always calculated to the fifth place, but are only given to the nearest number in the fourth, as this usually only affects the third place of the molecular rotations, which is not of much importance.

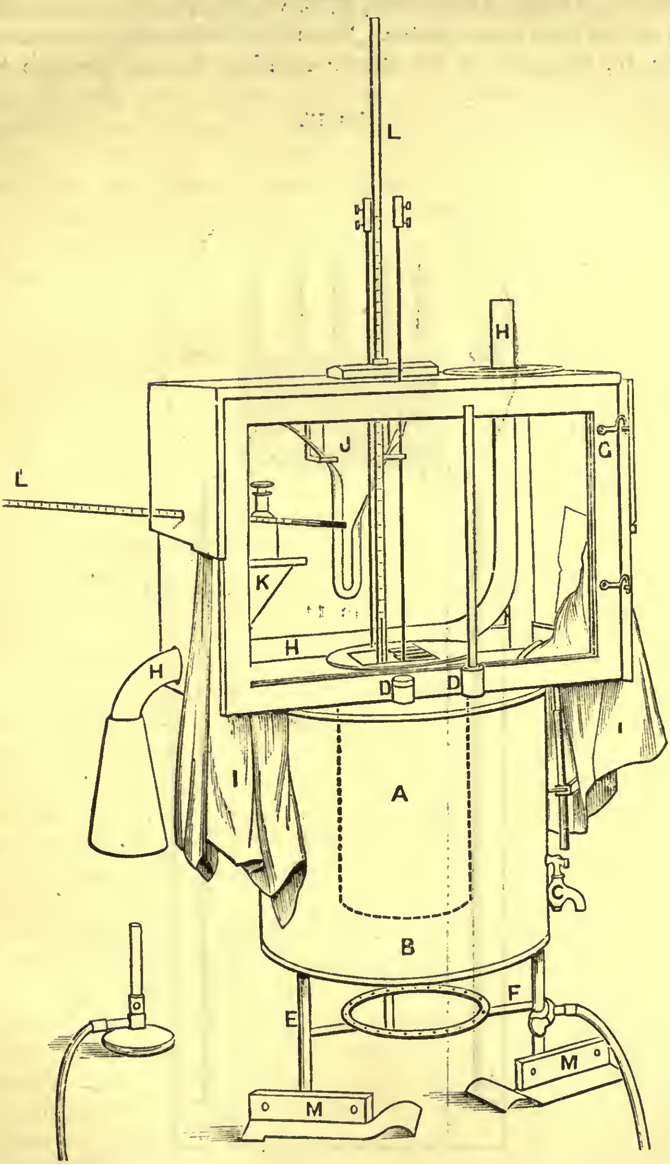
When determining the densities of substances, those of mixtures and solutions excepted, they have been generally taken at three or more temperatures, usually at 4°, 15°, and 25°, often also at 20°. The results have then been plotted out, and a curve drawn to the points, so that the density at any temperature within the limits of the determinations could be easily picked out when required. This method of plotting out the results is very useful, as it draws attention to any important errors, if they exist, either in the determinations or the calculations, as the curve would then be of an abnormal shape. In many cases the determinations have been made at a large number of different temperatures, nearly up to the boiling point of water; these results have likewise been plotted out and formed into curves. In a few cases, these long series of densities have been determined with the intention of studying some point connected with the rotations, and as, subsequently, this has not been deemed necessary, they were not required for this paper. All the densities were, however, made with much care, and with substances over which much time and trouble had been expended in order to get them as nearly pure as possible, and they have been given, as it was thought they might be useful to other experimenters. There is no doubt, however, that where very great accuracy is required in researches in which the densities take part in the calculations, that it is desirable that they should be determined with the actual specimens of the substances to be used; for very few products are really quite pure, and it often happens that the effect on the density of small amounts of impurity causes their influence on other properties to be neutralised, or nearly so, the results obtained being much nearer the truth than if the densities obtained by the examination of other specimens were employed.

For the purposes of this investigation, the densities of liquids and of fused solids have had to be determined, and for the latter a special apparatus had to be devised. It is evident that a substance melting above the ordinary atmospheric temperature cannot have its density taken by simply placing the density tube containing it in a water bath of the required temperature, because the small quantities in those parts of the capillary tubes which are exposed to the air would solidify, and thus seal the density tube, and if the temperature were raised burst it. It was necessary, therefore, to provide an arrangement in which the atmosphere above the bath should be heated to at least a few degrees above the fusing point of the substance, or, still better, to the temperature at which the determinations were to be made, because the mercury column of the thermometer which would be heated by this hot air would not then require to be corrected for temperature; moreover, the small quantities of substance in the capillaries would also be heated to the same temperature as that in the U-tube itself; these conditions would also be very suitable in the case of ordinary liquid substances when their densities at high temperatures were to be determined. Another important point to be attended to is that of regulating the temperature of the bath in which the density tubes are placed. As a great variety of temperatures somewhat quickly succeeding one another, had to be used in these determinations, no special arrangements, such as are often used to maintain a constant temperature for a long time, were of any value; it was necessary, however, that some means should be provided to keep the temperature constant at any desired point sufficiently long for the substance in the density tube to attain that of the bath. The following apparatus, shown in Fig. 13, was devised, and has been found to fulfil these conditions, although, of course, the difficulty of keeping the temperature quite constant to one or two hundredths of a degree increases as it rises.

The thermometers used were graduated to the one-fiftieth of a degree, and each had a range of 25°, so that four were required to indicate from zero to 100°. The Kew corrections were used, and were twice made at dates a few years apart. These were plotted out, and curves drawn to them, so that the correction required for any temperature could be easily picked out.

In Fig. 13, the bath or inner vessel for the density tubes is marked by the dotted line, and lettered A, and is seen in section, looking at it sideways, in Fig. 14. It is 21 cm. deep, and 13 cm. wide, and is provided with two stirrers, A, A, one on each side; these are prevented from

FIG. 13.



coming in contact with the density tubes by two wide strips of copper, B, B, perforated with some large holes, so as not to interfere with the thorough mixing of the water in the bath; the stirrers are moved perpendicularly almost the whole distance from the top to the bottom of the vessel, by means of the rods, C, C, which are worked from a long beam driven by a water motor. The top of this vessel is represented by Fig. 15, the rods of the stirrer working through the two holes,

FIG. 15.

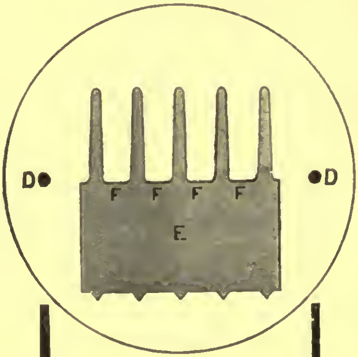
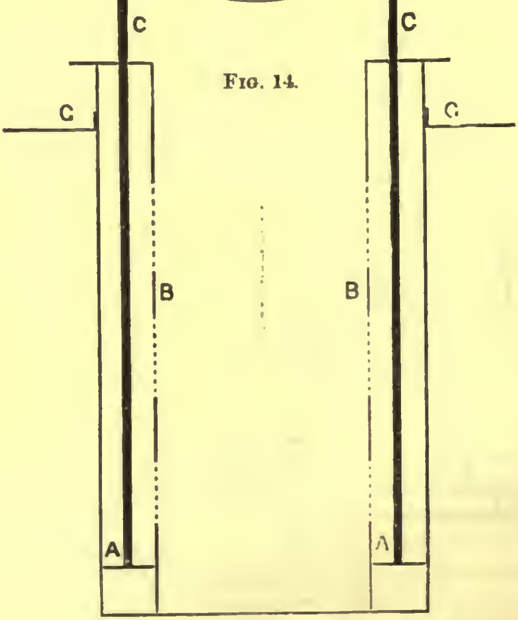


FIG. 14.



D, D. The square opening, E, for the admission of the density tubes, is provided on one side with four projecting pieces, F, F, F, F, and on the other with five notches, so that by this means five density tubes may be used at one time, and kept separate from each other, the capillary tubes with the bulbs being placed in the spaces between the projecting pieces, and the others in the notches. This vessel is also provided with a flange, G, G.

On referring again to Fig. 13, it is seen that the inner vessel just described passes through an aperture in the top of the outer one, B, and rests on the flange, by which it is fixed in its place by means of screws, the joint being made airtight with red lead putty. This outer vessel, B, is 27 cm. deep, and 31 c.c. in diameter, and is provided with a tap, C, by which it can be emptied; it has also two small apertures in the top, D, D, one for a thermometer, and the other for the introduction of water, and also at the back, near the top, there is another small opening for the escape of steam. This vessel stands on a tripod, E, provided with a ring gas burner, F, which can be raised or lowered at will.

The upper part of the apparatus consists of a chamber, the front and back of which are made of glass, and the top and sides of wood. The top of the vessel B, forms mainly the floor, the rest being made of sheet copper. The end of this chamber, on the right hand side, is hung on hinges, and thus forms a door G, through which the density tubes may be placed inside, or removed, as required. A copper tube, H, H, H, about 2·2 cm. internal diameter, and bent twice at right angles in opposite directions, and also provided with a funnel-shaped end, is fitted to this chamber, so that it may be used as a flue for heating it, the source of heat being a Bunsen burner; this flue is kept from contact with the woodwork by means of asbestos cardboard. The chamber is provided with large, chamois leather sleeves, I, I, on each side, through which the arms can be passed; these can be doubled in when the apparatus is being heated, so as to more perfectly stop up the openings, and thus avoid loss of heat. A rack J, on which to hang the density tubes, is provided at the back part of the chamber, and also a small shelf K, on which the bottle containing the fused substance to be examined can be placed and kept hot. The thermometer L, for registering the temperature of the bath passes into it through the top of the chamber, as also do the rods of the stirrers, the former being fixed in its place by means of a cork. A thermometer L′, passing nearly horizontally through the left side of the chamber, is used to give approximately the average temperature of the air it contains, so that, if necessary, correction can be made for the mercury column of the thermometer used for the bath. Should the column of the latter project any distance above the top of the chamber, a second thermometer can be used outside for making the required correction.

This apparatus has been used for all kinds of density determinations from about 10° or 15°, according to the atmospheric temperature, up to nearly 100°. For temperatures of about 4°, a simpler arrangement has been used, which is described further on.

When using this apparatus, water is first poured into the outer vessel, until within about half an inch of the bottom of the inner one, or bath, and this is then heated, if necessary, until the thermometer shows approximately the temperature at which the determination is to be made. The bath itself is then filled with water of about the desired temperature, and the stirrers set in motion; if the temperature to be used differs much from that of the atmosphere, the Bunsen burner under the flue is lit so as to heat the air of the chamber to approximately the same temperature, a few degrees difference between this and the bath having no practical influence on the determination. The density tube containing the product under examination is next placed in the bath, the temperature of which is then accurately adjusted by the introduction of small quantities of hot or cold water. The level of the liquid in the density tube is now brought approximately down to the mark, and, after resting a few minutes, finally adjusted. The tube is then removed, carefully dried, and, when it has acquired the temperature of the balance room, weighed.

In making determinations much above the ordinary temperature, the moist air in the outer vessel requires to be kept somewhat hotter than that of the bath, and increasingly so as the temperature rises. With the water well boiling in the outer vessel, and the air chamber heated to about 100°, the bath can be kept at about 99°.

When working with fused substances, the density tubes have to be filled in the chamber, previously heated to above their fusing points. To do this, the bottle of fused product is placed on the shelf, and its stopper removed, the density tube is also hung on the rack until sufficiently heated, the door of the chamber being closed. After a short time, the arms are passed through the leather sleeves, one end of a piece of fine vulcanised tubing, 2 or 3 ft. long, being also drawn in; this is then attached to the capillary bulb of the density tube, the other end being held in the mouth. The bottle of melted substance is next removed from the shelf, the free end of the density tube inserted into it, and the substance sucked into the tube, which, when filled, is placed in the bath previously heated to the desired temperature, the vulcanised tube is removed, and the usual adjustments made. The door is then opened, and the Sprengel tube removed, dried, and weighed. Before commencing a second determination at a higher temperature with the tube filled with the substance, which has now become solid by cooling, care must be taken not to burst it, as the capillaries are generally sealed. Usually, if it is suspended in the rack in the chamber, the capillary tubes being narrow, the substance in them fuses first, but it is safer first to heat them and the upper part of the U-tube very carefully with a lamp before putting it into the rack; it should then be left until all the substance is melted. If an attempt is made to facilitate the melting by means of a lamp, or by placing it in the hot water bath, a good deal of substance is often lost, owing to the air which fills the cavities of the solidified product being rapidly liberated and forming large bubbles, which occupy the entire diameter of the tube, and, as they rise, force some of the fused product out of the tube; if, on the other hand, it is left in the rack, the melting is gradual, and the air bubbles being small, usually escape without carrying the substance with them, at all events to any great extent.

The determination of the densities of substances with high melting points, such as acenaphthene, for instance, which fuses at 95°, is not very easy; the temperature of the chamber has to be about 100°, and the bath approaching this temperature, so that the atmosphere in which the filling of the tube has to be conducted is rather trying to the hands—especially as it consists largely of steam; moreover, on the least lowering of temperature the capillary tubes become blocked; this also used to occur, sometimes when the filled tubes were placed in the bath, owing to a little cold air getting in through the chamois leather sleeves, and, of course, if it happens, it endangers the density tube, as a little expansion would cause it to burst. To avoid this, when determining the densities of substances with high fusing points such as the above, two small screens, Fig. 13, M, M, were made of pieces of moderately thick sheet copper, about 17 c.m. long and 7·0 wide, turned up at right angles on one side, and the ends so bent that they would rest on the copper flue of the chamber; they were made right and left handed, and placed across the chamber from front to back, and on either side of the bath. The turned-up edges thus act as screens to shield the capillary tubes from draughts, and at the same time these pieces of copper are heated somewhat above that of the chamber by conduction from the flue, so that the substance in the capillaries is kept fused by radiation. The turned up sides of these pieces of copper are covered on one face with asbestos cardboard, in order that the hands may not come in contact with the hot metal. If oil or glycerine were employed, no doubt manipulation at high temperatures would be easier than when water is used, as the heated air in the chamber would be dry; but it is troublesome to change the liquid in the bath, and, moreover, the high specific heat of water is a great advantage.

For determining densities at low temperatures, such as 4°, the apparatus used was precisely the same as the inner vessel or water bath of the above, including the stirrers, &c.; this was fitted into the lid of a square box standing on legs, in the centre of which a cylinder, made of perforated zinc, was fixed, a little larger than the bath, so that when ice was packed around the zinc cylinder it would not come in contact with the inner vessel. The box was also provided with a syphon-shaped tube fixed in the bottom to drain off the water produced by the melting ice. With this arrangement, a temperature of 4° or lower could be easily maintained for some time, a very little warm or ice-cold water being added if the temperature were inclined to fall or rise.

As the density tubes, when removed from a bath of lower temperature than that of the atmosphere, cannot be dried, they were placed in water 2° or 3° above that of the balance-room for a short time previous to wiping them, and afterwards left to cool. With tubes which have been removed from a hot bath, much time may be saved by placing them in a bath of this kind before drying them.

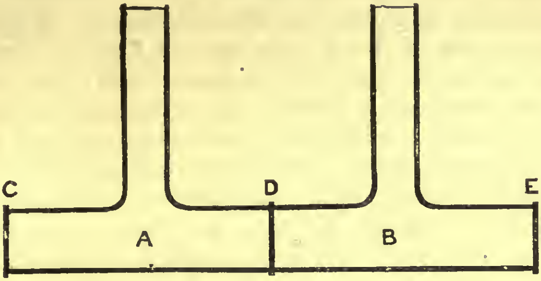
Magnetic Rotation of Mixtures.

As will be found further on (pp. 1093—96, 1119), certain groups and elements having *low* rotations, when they enter into molecules with relatively high rotation, sometimes yield products having lower rotations than would be expected from such displacements; at first it was thought that the lower rotating product in some way reduced the influence of the higher one. The consideration of this made it appear of interest to examine mixtures of *compounds*, both those having greatly varying, and also those with identical, or nearly identical, specific rotations, in order to ascertain whether mixtures of molecules of different and of similar rotatory power would simply give additive results or not, or whether, when there is a considerable difference in their rotations, the result would be lower than that of the sum of the two.

First of all it was thought advisable to examine in the magnetic field some of the substances to be used in these mixtures in such a manner that the light, after passing through one of small rotation, should then pass through the other, or *vice versâ*, subsequently examining the effect of the two when mixed. For this purpose a specially divided tube was made, as shown in Fig. 16, consisting of two halves, A and B, of exactly the same length, namely 50 cm., separated by a glass disc D, the ends also being closed with glass discs C, E.

This divided tube, with its ends, measured 105 mm. in length; when using it, one-half was filled with one substance, and the other with the other, and the combined rotation determined; equal volumes of the same substances were then mixed, the density of the mixtures determined, then both halves of the tube were filled with it, and the rotation again determined.

FIG. 16.



As was to be expected, the result of the examination of the two substances, unmixed, was simply additive. The following are the examples.

Substances.	Mol. rot. found.	Mol. rot. calculated.
Carbon bisulphide, equal lengths at 15°. Ethylic nitrate, ,, ,,	13·015	13·012
Ethylic benzoate, ,, ,, Ethylic butyrate, ,, ,,	20·848	20·877
Isoamylic iodide, ,, ,, Isoamylic oxide, ,, ,,	20·385	20·399

Most of the mixtures examined consisted of equal volumes of each of the constituents at 15°; this would correspond to equal lengths in the measuring tube. Of course it was necessary to make and examine the mixtures at one and the same temperature, for, as the substances expand differently when heated, their volumes would not be equal at any other temperature. To prepare them as accurately as possible, the several products were carefully weighed, the weights of equal volumes at 15° being calculated from the densities at 15°.

On mixing liquids, a change of density usually occurs, but in most of the mixtures examined this has been small, sometimes being due to contraction, at others to expansion. We know very little of the altered condition of the molecules when change of density occurs on mixing different liquids, but probably in the mixtures examined the relative volumes remained almost unchanged. These changes of density influence the relationship of the specific rotation, and must, of course, be taken into account before they can be compared, first by dividing the specific rotation of the unmixed products by the *average* of their densities, and then by doing the same with that of the mixtures—their found densities being employed—the results will then probably be comparable within experimental errors. This method of calculation was at first adopted, but afterwards it was thought better to calculate the molecular rotations, and thus treat substances, when unmixed, and when mixed, as a whole; for instance, equal volumes of carbon bisulphide and ethylic nitrate at 15° will have the composition of CS_2 + 0·733 of a mol. of $EtNO_3$. Knowing the molecular rotation of these two substances, that of the mixture can easily be calculated; it is 13·002. To calculate the molecular rotation from the specific rotation of the unmixed products determined in the double tube, namely, 1·9605, the average of the densities of carbon bisulphide and ethylic nitrate is first ascertained; this is 1·1939; then the molecular weight for these products in the above proportions is calculated, and is found to be 142·67. From these data the molecular rotation can be determined in the usual manner, and comes out as 13·015—practically the same as the calculated. With the mixed products, the specific rotation is 1·7907, the density of the mixture 1·1753, and the molecular weight the same as for the unmixed products; these numbers give 12·072 as the molecular rotation, showing that a considerable reduction takes place when the two substances are mixed.

The results obtained in this inquiry are given in the following table. In the first seven, mixtures containing equal volumes were employed; in the eighth, two volumes to one, and in the last three they were in molecular proportion.

From the results it is evident that in all cases where the specific rotations of the products, used for the mixtures, lie wide apart (as can be seen by their ratios, given in column 7 of the table), the molecular rotations are below the calculated, and, roughly, the amount of variation increases with the divergence of the molecular rotations, as seen by comparing the 1st, 6th, and 7th. Whether the others would come into closer accord by a more critical determination is uncertain, because the mixtures, although consisting of compounds not likely to have chemical action on each other, nevertheless contain different kinds of groups, and these may not all behave in a similar manner. In the last two examples, substances have been used with specific rotations which are nearly identical, and the molecular rotations they give are practically the same as the calculated.

These results, therefore, bring out the remarkable fact that these mixtures of substances of very different specific rotations give lower results than the rotations calculated from their separate constituents; and also, from the last two, that when they are very similar, they give simply additive results corresponding to the rotations of their separate constituents. It is evident, therefore, that there is an interference of

Magnetic Rotations of Mixtures.

Volumes.	Substances.	Mol. comp.	Mol. rot. found.	Mol. rot calc.	Diff.	Ratio of sp. rots.	Density 15/15°.	Diff.	Effect.
1 : 1	Ethylic phthalate and ethylic oxalate	1 : 1·464	26·504	26·633	−0·129	1 : 0·578	Av. unmixed, 1·1055 mixed, 1·1063	+0·0008	Contraction.
1 : 1	Isoamylic iodide and isoamylic oxide...	1 : 0·644	20·164	20·399	−0·235	1 : 0·550	Av. unmixed, 1·1487 mixed, 1·1488	+0·0001	”
1 : 1	Ethylic benzoate and ethylic butyrate............	1 : 1·084	20·651	20·877	−0·226	1 : 0·507	Av. unmixed, 0·9692 mixed, 0·9716	+0·0024	”
1 : 1	Ethylic benzoate and ethylic formate	1 : 1·802	20·061	20·281	−0·220	1 : 0·457	Av. unmixed, 0·9937 mixed, 0·9948	+0·0011	”
1 : 1	Benzene and heptane............	1 : 0·606	15·732	15·936	−0·204	1 : 0·413	Av. unmixed, 0·7868 mixed, 0·7810	−0·0058	Expansion.
1 : 1	Dimethylaniline and isoamylic oxide..........	1 : 0·621	29·389	29·837	−0·448	1 : 0·307	Av. unmixed, 0·8714 mixed, 0·8726	+0·0012	Contraction.
1 : 1	Carbon bisulphide and ethylic nitrate	1 : 0·733	12·072	13·012	−0·936	1 : 0·210	Av. unmixed, 1·1939 mixed, 1·1753	−0·0186	Expansion.
2 : 1	Carbon bisulphide and ethylic nitrate	2 : 0·733	22·437	23·744	−1·307	1 : 0·105	Av. unmixed, 1·2199 mixed, 1·2030	−0·0169	”
	Dimethylaniline and dipropylamine...	1 : 1	22·588	22·897	−0·309	1 : 0·306	Av. unmixed, 0·8525 mixed, 0·8520	−0·0005	”
	Nitrobenzene and isobutylic benzoate.............	1 : 1	25·418	25·404	+0·014	1 : 0·9848	Av. unmixed, 1·1064 mixed, 1·0782	−0·0282	”
	Methylic salicylate and benzonitrile..	1 : 1	26·110	26·119	+0·009	1 : 1·0422	Av. unmixed, 1·0996 mixed, 1·1101	−0·0105	Contraction.

the molecules of the substance of lower rotation with those of the higher, as though the polarised light passed through a larger number of the former than of the latter, selecting the shorter path. This is very remarkable and interesting from a theoretical point of view, and is important practically as showing that in examining the rotation of solutions it is necessary to employ a solvent with a specific rotation as near that of the dissolved substance as possible. In this paper an endeavour has been made to do this as far as practicable; with substances of this kind it is not, however, always possible to do so, and, therefore, it is necessary to remember that when the solvent has a considerably lower rotation than the substance dissolved, the rotation of the latter will appear somewhat lower than it actually should be.

Aqueous and Alcoholic Solutions.

Water and alcohols do not always behave like other solvents which are more neutral in their character, there being a greater tendency on their part to the formation of chemical compounds with other substances; it has been thought best, therefore, to consider them separately.

In the fatty series, many aqueous solutions have been examined at different times; amongst those in which no chemical union appears to take place are alcohol, the monobasic acids of the fatty series (Trans., 1886, **49**, 778, &c.), and some of their halogen derivatives (Trans., 1894, **65**, 421, &c.), also the dibasic acids, such as malonic, glutaric, maleïc, and citraconic acids (Trans., 1888, **53**, 421, &c.). Now, in most of these compounds the specific rotations are not very different from that of water, and, therefore, very little change would be likely to result from their being dissolved in it.

The specific rotations of the bromacetic acids, however, are a good deal larger than that of water, bromacetic acid being about 1·400, whilst dibromacetic acid is about 1·600, and tribromacetic acid about 1·800, and yet the aqueous solutions gave for these acids the same rotations as were obtained from the pure compounds, just as in the case of bromacetic acid, or in the solution of the acid in a solvent having a similar specific rotation, as tribromacetic acid, for instance, in ethylic butyrate (Trans., 1894, **65**, 425 and 427). It must be borne in mind, however, that all these aqueous solutions were very concentrated, and, therefore contained but little water, about 20 per cent., and this would reduce the influence of the divergence of the specific rotation very materially; still it might have been expected to manifest itself to some extent if water behaves in the same manner as the other solvents used in the foregoing mixtures.

In the aromatic series, examples exist of mixtures with water where no other chemical union is probable; these are phenol, paracresol, resorcinol, pyrocatechol, and pyrogallol. The proportion of water in the first two is but small, as in both cases the mixture of the phenols and water which was used could only contain them in single molecular proportions. The phenol solution contained 16·07 per cent, and the paracresol 14·28 per cent. The following are the results.

	Mol. rot. $C_6H_6O + OH_2$.	Mol. rot. $C_7H_8O + OH_2$.
Calculated..............	13·140	13·869
Found..................	13·095	13·768
Reduction..............	0·045	0·101

If, for the sake of comparison, these results are calculated for 10 per cent. of water, phenol gives 0·028 and paracresol 0·071 difference in rotation.

The specific rotation of phenol is about 2·46, and that of paracresol 2·22, which is considerably above that of water; it would seem, therefore, that in these cases water does act to some extent like other solvents, reducing the rotation when the mixture contains a compound of higher specific rotation than itself.

With respect to resorcinol, which is the only other compound from which data have been obtained, the rotation of the dry substance could not be determined; two solutions of different strengths were, therefore, examined, one containing 63·583 and the other 30·285 per cent. of resorcinol, and 36·417 and 69·715 per cent. of water respectively. These differed in rotation by 0·174 for the 33·298 per cent. of water by which they vary, or 0·052 for each 10 per cent. of water, a result nearly the average of that of the two phenols, which amounts to 0·049. This is calculated on the assumption that the rotations differ equally for successive dilutions; this, however, may not be the case. The specific rotation of resorcinol should not be very different from that of phenol, but, of course, a great deal higher than that of water.

In the case of the two amines isobutylamine and piperidine, which have specific rotations very nearly the same as that of water and not very different from that of alcohol, it would be expected that the rotation of the product obtained when these substances were mixed with water or alcohol would be normal, but in each case there is a reduction (Trans., 1889, **55**, 735, 736). It may be noted, also, in making these mixtures, that considerable heat is evolved, and that there is an increase of density, all pointing to chemical union.

In the aromatic series, benzylamine, mixed with its own volume of water, was examined, and paratoluidine mixed with 2 mols. of alcohol. In the former case, much heat was given out on making the mixture the density, also showing that a good deal of contraction occurred. The rotation likewise shows a considerable reduction, thus.

Mol. rot. of $C_7H_7{\cdot}NH_2 + 6{\cdot}022\ OH_2$ cal. = 19·687
Found .... 19·154

Reduction .... 0·533

In the case of paratoluidine—

Mol. rot. of $C_7H_7{\cdot}NH_2 + 2C_2H_6O$ calc... 21·748
Found .... 21·023

Reduction .... 0·725

These results correspond to those of the fatty bases with water and alcohol, but the differences are larger, as might be expected; this may be due to two influences: namely, the chemical union of the base with water or alcohol, and then, also, to the influence of the low rotation of the rest of the solvent on the higher rotation of the product in solution.

Effect of Variation of Temperature on Magnetic Rotations.

In my early papers on magnetic rotations, I was led to consider that the molecular rotations of substances were the same at all temperatures, from the fact that no practical differences were noticed in the numbers obtained at the atmospheric temperature in winter and summer, the specific rotation apparently simply changing with the density. I was aware that De la Rive (*Ann. Chim. Phys.*, 1871, **22**, 31) believed that there was a difference, but thought that this was due to his methods of measurements being less perfect than those now in use; moreover, the data on which he founded his opinion were evidently faulty, as will be seen further on. Some ten years ago, when commencing the examination of aromatic compounds, it was noticed that substances with large rotations, like iodobenzene, appeared to give fluctuations in their rotations with large changes of atmospheric temperature, and this induced me to make direct experiments at widely different temperatures in order to test this point. The first substances examined were water and iodobenzene, and it was found that although the rotation of water changed apparently only in proportion to its expansion with heat, or, in other words, with its density, iodobenzene changed to a greater extent; and, on examining other substances, it has since been found that in all cases the rotations change with alterations of temperature to a greater extent than the density, water excepted, the amount varying with different compounds. The first time this was referred to was in a paper on "Saturated and Unsaturated Bibasic Acids and their Derivatives," in which it is stated that "it is found that the molecular rotation of a substance is not quite constant for all temperatures, falling off a little with rise of temperature" (Trans., 1888, **53**, 598); since then attention has been frequently drawn to this subject, especially in a paper on the "Refractive Power of certain Organic Compounds at different Temperatures" (Trans., 1892, **61**, 290 and 309).

This alteration,* which is in excess of the change of density, is found by subtracting the molecular rotations determined at temperatures wide apart, and then calculating the product for 100° for the sake of making comparisons. This it is proposed to call the *Temperature Difference*. Calculating the results for 100° may be objected to, and probably it is not strictly correct to do so, but, judging from the determinations which have been made, the coefficient of change does not appear to vary to any very great extent for different temperatures; or, at any rate, not sufficiently to seriously affect the generalisations based upon the numbers thus obtained, as the following results will indicate.

Temperature Differences for Varying Ranges of Degrees, also calculated for 100° *for comparison.*

Chlorobenzene....	0·252	diff. on mol.	rot. for	66·5°	= 0·379	for 100°
,, ...	0·278	,,	,,	74·0	= 0·376	,,
Bromobenzene....	0·317	,,	,,	69·6	= 0·455	,,
,, ...	0·332	,,	,,	77·6	= 0·428	,,
Toluene	0·223	,,	,,	40·6	= 0·543	,,
,, ...	0·353	,,	,,	67·6	= 0·518	,,
Ethylic phthalate.	0·187	,,	,,	56·0	= 0·334	,,
,, ,, ..	0·257	,,	,,	71·4	= 0·358	,,
Pseudocumene....	0·212	,,	,,	36·6	= 0·598	,,
,, ...	0·438	,,	,,	71·5	= 0·607	,,
Heptane	0·152	,,	,,	55·5	= 0·274	,,
,, ...	0·208	,,	,,	72·1	= 0·287	,,

It will be seen that some of the differences at the higher temperatures are slightly lower than those at the lower temperatures, whereas in others the reverse is the case; this may arise from experimental errors, and must be decided by future determinations.

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* Messrs. Rodger and Watson (*Phil. Trans.*, 1895, **186**, 654), in their remarks in reference to the methods of calculating molecular rotations, and the use of water as a unit of reference, do not seem to have noticed that the fact of molecular rotations varying with changes of temperature has been recognised for a long time, as shown above, and that it was also not lost sight of when considering the subject of tautomeric change (see Trans., 1892, **61**, 809, 813, 822, 824, 832). Moreover, the difference of molecular rotation for changes of the latter kind which have up to the present been considered, are also usually much larger than those for ordinary temperature differences.

In further considering the results which have been obtained, it has been thought best to commence with those relating to water, which is always used as the unit of comparison in my determinations of magnetic rotations.*

In previous papers, it has been stated that the magnetic rotations of water at different temperatures simply follow the change of density. The results on which this was based are given below. In these determinations, the magnet and pole pieces were heated, as well as the water under examination, by the circulation of water of different temperatures through the channels provided for this purpose. The average of the lowest determinations is 16°, and this is taken as 0·999, the density of water at this heat, the rotation at 4° being considered as unity. The following are the results obtained.

Comparison of the Magnetic Rotation of Water at various Temperatures, with its Density, the Magnet being heated.

t.	Rotation.	Density.	Rot./*d*.
4·0°	—	1·000	—
16·0	0·999	0·999	1·000
40·5	0·993	0·992	1·001
45·4	0·990	0·990	1·000
54·0	0·986	0·986	1·000
62·0	0·983	0·982	1·001
66·5	0·982	0·980	1·002
73·0	0·976	0·976	1·000
81·7	0·971	0·971	1·000
86·0	0·970	0·968	1·002
89·0	0·966	0·966	1·000
89·7	0·966	0·965	1·001
91·0	0·966	0·965	1·001

From these numbers it appeared, as I have already stated, that the change in the rotation is as nearly as possible identical with the change of density, as seen from the last column.

Since these determinations were made, Messrs. Rodger and Watson (*Phil. Trans.*, 1895, **186**, 648) have made some very careful experiments on the magnetic rotation of water, in relation to its absolute values, at temperatures up to its boiling point, and also of some other liquids, but using a large coil instead of an electromagnet, as I did.

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* The formula used for calculating the molecular rotation of a substance from the observed is—

$$\text{Mol. rot.} = \overset{\text{Substance.}}{\frac{r \times Mw}{d}} \div \overset{\text{Water.}}{\frac{r' \times Mw'}{d'}} = \frac{r \times Mw \times d'}{r' \times Mw' \times d}.$$

For further particulars, see Trans., 1884, **45**, 579.

On comparing our numbers, it was found that they did not quite agree, their measurements showing that the alteration in the rotation of water did not strictly follow that of density, as the foregoing results seemed to show. The difference between our results for water at its boiling point was about 0·7 per cent., being but little more than 2′ on my readings. The only way of accounting for this discrepancy was that some slight change occurred in the magnetic field of my apparatus when the magnet was heated, although the battery current was kept constant and a magnetometer influenced by the general radiation from the magnet showed no practical variation, a very minute lowering being noticed on two occasions only.

To investigate this matter, two methods were employed; one was to measure water at about 15°, first with the magnet cold, and then when it was heated; the other was the reverse of this, namely, to measure water at 15° and near its boiling point, the magnet being kept cold. The results of the measurements made in these different ways showed that the electromagnet when heated has not exactly the same field as when cool, notwithstanding the electric current is kept so as always to give the same deflection of the galvanometer, and is not sufficiently powerful to fully saturate the iron. Determinations were therefore made, keeping the magnet cold and heating the water, avoiding the loss of heat from the conduction of the pole pieces by interposing a screen of bad conducting material; numbers were then obtained analogous to those of Rodger and Watson. The following is a comparison of some of the results, water at 0° being taken as 1000.

t.	Perkin.	Roger and Watson.
45·4°	0·9918	0·9923
61·5	0·9858	0·9867
81·0	0·9773	0·9776
99·5	0·9657	0·9663

Our results, therefore, agree closely, and as these numbers are slightly larger than the densities of water at the same temperatures, they show that the rotation of water does not fall exactly with its density, but lags behind by about 0·8 per cent. at 100°.

The following table, calculated from Rodger and Watson's results, shows the relation of the rotation of water to its density for every 20° between 0° and 100°.

t.	Rot.	Rot./*d*.
0°	1·0000	1·0000
20	0·9985	1·0000
40	0·9939	1·0015
60	0·9870	1·0038
80	0·9779	1·0061
100	0·9664	1·0084

Further observations on these results will be found on p. 1071.

De la Rive obtained numbers with water the reverse of the foregoing; moreover, in his examination of ethylic iodide he found that the rotation followed the density, and, as this also is not the case, the evidence on which he assumed that the rotation did not in all cases vary as the density was misleading.

Most of the results in this paper obtained at temperatures above the atmospheric were made with the magnet in a heated condition; the change in the value of the magnetic field above referred to does not, however, influence the measurements, because they are all relative to water measured under the same conditions.

The effect of a comparison between the rotation taken at high temperatures of substances which do fall more rapidly than their densities, and water, which behaves in the opposite manner, is simply to slightly reduce the result.

After finding that the rotations were influenced by changes of temperature to a greater extent than could be accounted for by the alteration of density, a large number of substances were examined to see if the *temperature differences*, as I propose to call them, were connected with any general law.

On studying the results, it was noticed that substances with large specific rotations gave larger temperature differences than those with small specific rotations; but, on arranging them in this order, it was not found that any regularity existed in this connection; the same want of agreement also obtained on arranging the differences in the order of their specific rotations divided by density. Comparisons were also made in respect of the temperature difference and the coefficient of expansion by heat, but no relation between the two was observable. At last it became apparent that each class of compound had its own kind of temperature difference. The results obtained have therefore been tabulated on this principle, the following particulars being given, namely, the specific rotations alone, and also divided by density, the molecular rotations, the temperature differences, the percentage change on the molecular rotations and on the specific rotations divided by density, which is the same in both cases. Fifty-four compounds have been examined in reference to the changes which occur in their rotations with variations of temperature.

On examining these tables, it is found, as might be expected, that the temperature differences are greater in the aromatic series than in the fatty series. It is also well to bear in mind that these differences, especially when small, represent but minute variations in rotations, and therefore, as previously pointed out, are more influenced by experimental errors than ordinary magnetic rotations; on studying the numbers, however, it is found that there is a closer analogy between the temperature differences of the members of each group of substances than is at first apparent, one of the principal causes being the difference in composition of the homologous compounds. It will be seen, on comparing them, that there is apparently a temperature difference corresponding with each difference of CH_2, and this consequently causes the compounds higher in the series to have larger differences than those lower in the series; for instance, in the fatty series, œnanthylic acid has a larger difference than propionic acid.

Effect of Variations of Temperature on the Rotations of Compounds of the Fatty Series.

Substance.	Sp. rot. 15°.	$\frac{\text{Sp. rot.}}{d.}$ 15°.	Mol. rot. 15°.	Diff. in mol. rot. for 100°.	Change per cent. in mol. rot. for 100°.
Heptane	0·9500	1·3799	7·666	0·288	3·763
Acetic acid	0·8016	0·7584	2·528	0·049	1·947
Propionic acid	0·8412	0·8425	3·464	0·034	0·981
Œnanthylic acid	0·9649	1·0459	7·554	0·113	1·497
Ethylic œnanthate	0·9480	1·0871	9·542	0·167	1·748
Chloracetic acid	—	—	3·882	0·032	0·824
Dichloracetic acid	1·1615	0·7395	5·300	0·067	1·271
Trichloracetic acid	—	—	6·473	0·110	1·700
Dipropyl ketone	0·9683	1·1795	7·471	0·178	2·387
Ethylic acetoacetate	0·9289	0·9003	6·502	0·071	1·093
Dimethylacetylacetone	0·9475	0·9907	7·045	0·064	0·909
Hydracetylacetone	1·0361	1·0361	5·871	0·050	0·852
Ethylene chloride	1·2564	0·9972	5·484	0·114	2·078
Octylic chloride	1·0802	1·2286	10·139	0·250	2·465
Propylic bromide	1·3733	1·0068	6·880	0·210	3·050
Octylic bromide	1·2517	1·1214	12·025	0·288	2·397
Ethylic iodide	2·2675	1·1632	10·082	0·394	3·905
Octylic iodide	1·6282	1·2136	16·182	0·474	2·929
Methylene diiodide	4·1731	1·2522	18·644	0·863	4·622
Pyrotartaric anhydride	0·9303	0·7516	4·759	0·091	1·921
Unsaturated Compounds.					
Ethylic citraconate	1·0645	1·0158	10·497	0·220	2·096
Citraconic anhydride	1·1139	0·9808	5·543	0·132	2·390

By taking all the available results obtained from homologous compounds of the fatty series, and then those of the aromatic series, and comparing them, probable values for CH_2 in both will be obtained, from which the temperature differences for other homologues may be estimated.

Effect of Variations of Temperature on the Rotation of Compounds of the Aromatic Series.

Substance.	Sp. rot. 15°.	$\frac{\text{Sp. rot.}}{d}$. 15°.	Mol. rot. 15°.	Diff. in mol. rot. for 100°.	Change per cent. in mol. rot. for 100°.
Nitrobenzene	1·6566	1·3671	9·361	0·124	1·327
Benzene	2·3053	2·6039	11·284	0·477	4·227
Toluene	2·0748	2·3785	12·157	0·530	4·395
Mesitylene	1·7412	2·0048	13·366	0·574	4·294
Pseudocumene	1·8498	2·0996	13·998	0·600	4·300
Diphenylmethane	2·5553	2·5547	23·845	0·621	2·604
Naphthalene	—	—	25·125	0·458	1·822
Ethylic hydrocinnamate	1·6697	1·6350	16·176	0·410	2·540
Ethylic phthalate	1·5448	1·3709	16·909	0·346	2·048
Ethylic benzoylacetate	1·7260	1·5384	16·411	0·590	3·612
Phenylic acetate	1·8506	1·7143	12·953	0·311	2·404
Phenylic œnanthate	1·5377	1·5660	17·923	0·477	2·661
Phenol	—	—	12·140	0·233	1·919
Thymol	1·8938	1·9344	16·120	0·348	2·158
Dimethylquinol	—	—	16·717	0·685	4·097
Trimethylpyrogallol	—	—	17·201	0·621	3·610
α-Naphthyl ethyl oxide	3·5877	3·3734	32·237	1·671	5·184
Benzaldehyde	2·1153	2·0145	11·864	0·373	3·144
Benzylic alcohol	2·1700	2·0666	12·400	0·222	1·780
Acetophenone	1·9517	1·8895	12·597	0·316	2·510
Benzophenone	—	—	23·371	0·689	2·948
Chlorobenzene	2·2268	2·0016	12·510	0·377	3·046
Bromobenzene	2·4932	1·6631	14·506	0·436	3·007
Iodobenzene	3·1024	1·6859	19·108	0·756	3·970
Parabromotoluene	—	—	15·167	0·440	2·901
Phenylic sulphide	3·2113	2·8710	29·668	0·996	3·356
Aniline	3·1905	3·1114	16·076	0·750	4·665
Dimethylaniline	3·2758	3·4048	22·888	0·936	4·089
α-Naphthylamine	—	—	37·478	1·561	4·165
Unsaturated Compounds.					
Allyl phenyl oxide	2·2672	2·3014	17·134	0·719	4·196
Cinnamic alcohol	—	—	17·940	0·601	3·352
Ethylic cinnamate	2·1577	2·0459	20·006	0·685	3·425

The following table shows these differences.

Substance.	Temp. diff. for 100°.	Diff. for CH_2.
Œnanthylic acid	0·113	0·079 ÷ 4 = 0·020
Propionic acid	0·034	
Octylic iodide	0·474	0·080 ÷ 6 = 0·013
Ethylic iodide	0·394	
Octylic bromide	0·288	0·078 ÷ 5 = 0·016
Propylic bromide	0·210	
	Average	0·016
Pseudocumene	0·600	0·070 ÷ 2 = 0·035
Toluene	0·530	
Mesitylene	0·574	0·044 ÷ 2 = 0·022
Toluene	0·530	
Thymol	0·348	0·115 ÷ 4 = 0·029
Phenol	0·233	
	Average	0·027

As usual, the difference for CH_2 is larger in the aromatic than in the fatty series; these, however, being very small, and obtained from a small number of examples, are probably not quite accurate; nevertheless, they appear to show the existence of temperature differences for the CH_2 group. It is quite likely that CH_2 and CH_3, displacing hydrogen, have not precisely the same values, but any variation due to this would probably be very small. In the examples given in connection with the fatty series, only differences for CH_2 occur.

If the paraffins be taken as the starting point of the fatty compounds, and benzene hydrocarbons of the aromatic compounds, their temperature differences for CH_2 will be useful in comparisons in relation to the differences of their derivatives.

From the temperature differences for CH_2, that of each of the paraffins can be estimated from that found for heptane, and may be represented thus.

Substance.	Estimated temp. diff. for 100°.
Octane	0·304
Heptane	0·288
Hexane	0·272
Pentane	0·256
Butane	0·240
Propane	0·224
Ethane	0·208
Methane	0·192

By displacing hydrogen in these paraffins by CO·OH or CO·OEt, and thus producing the corresponding acids or ethereal salts, it is found that the temperature difference is greatly reduced, thus.

Substance.	Temp. diff.	Reduction of temp. diff.
Propane (estimated)........	0·224	0·190
Propionic acid	0·034	
Heptane	0·288	0·175
Œnanthylic acid	0·113	

Carbonyl when displacing hydrogen so as to form a ketone also reduces the temperature difference; thus, in the cases of dipropyl ketone and the diketone dimethylacetylacetone, the following differences are found.

Substance.	Temp. diff.	Reduction of temp. diff.
Heptane	0·288	0·110
Dipropyl ketone	0·178	
Heptane	0·288	0·224 ÷ 2 = 0·112
Dimethylacetylacetone......	0·064	

In ethylic acetoacetate, where both CO and CO·OEt displace CH_2 groups, the reduction is also very great, as might be expected.

Hydroxyl also appears to act in a similar manner to the above, because in hydracetylacetone, which contains both OH and CO, the temperature difference, if compared with that of pentane, shows a reduction of 0·206, which is greater than that resulting from the influence of CO alone, although very nearly the same as that of COOH, as can be seen on comparing propane with propionic acid.

The CO·O·CO group displacing two CH_2 groups in pentane, and thus giving pyrotartaric anhydride, also causes a considerable reduction in the temperature difference, amounting to 0·165 less than that of the paraffin.

In the aromatic series, analogous results are observed; thus, on comparing the temperature differences of toluene and benzaldehyde, a reduction of 0·157 is found; in the case of the ketone, acetophenone, when it is compared with the *estimated* temperature difference of ethylbenzene, the lowering is still greater, amounting to 0·258.

The temperature difference of benzophenone when compared with that of diphenylmethane is seen to be the higher of the two, and therefore appears to be an exception, but, owing to the very high molecular weights of these substances, it is possible that their temperature differences may not have been determined with sufficient accuracy for this comparison, although their rotations were in both cases twice determined at high temperatures. It is also well to remember that the rotation of benzophenone is not quite what might be expected (see p. 1093).

The displacement of hydrogen in benzene and toluene by hydroxyl, forming phenol and benzylic alcohol, causes a reduction of the temperature difference, thus

Substance.	Temp. diff.	Reduction of temp. diff.
Benzene	0·477	0·244
Phenol.....................	0·233	
Toluene	0·530	0·208
Benzylic alcohol............	0·222	

the difference in the case of the phenol, as might be expected, being larger than that of the alcohol, where the hydroxyl is associated with the fatty group. The temperature difference of thymol is also much smaller than that of the corresponding hydrocarbon, which should be about 0·600, and if this be correct, the difference would amount to 0·252, or very nearly the same as that in the case of phenol.

The temperature differences of ethylic hydrocinnamate, and ethylic phthalate are also low, so that, as in the fatty series, the groups CO·OH, and CO·OEt evidently influence the temperature differences in an analogous manner.

The temperature differences due to the displacement of hydrogen in hydrocarbons by NH_2 and $N(CH_3)_2$ groups have not been determined in the fatty series, but in the aromatic the results are in the opposite direction to those considered above, inasmuch as they cause the temperature difference of the amines formed to be greater than that of the hydrocarbons themselves; thus, aniline has a temperature difference of 0·750, whilst that of benzene is only 0·477, or an increase of 0·273. That of dimethylaniline is much larger, namely, 0·936, and α-naphthylamine gives no less than 1·561, or rather more than twice that of aniline.

The unsaturated compounds of both the fatty and aromatic series give temperature differences larger than those of the saturated series; thus, that of citraconic anhydride is larger than that of pyrotartaric anhydride. Ethylic citraconate evidently has a high temperature difference, as it is greater than that of ethylic œnanthate, and this is no doubt higher than that of ethylic pyrotartrate, the substance with which it must be compared. In the aromatic series, it is found that ethylic cinnamate has a considerably higher temperature difference than ethylic hydrocinnamate, and cinnamic than benzylic alcohol, allowing in the latter case for the difference of $CH_2 \times 2$, which would make them comparable. Allyl phenyl oxide also gives a very high number.

In reference to compounds containing halogens, chlorine, when displacing an atom of hydrogen in a compound, appears to have a reducing influence on its temperature difference; this is seen in the case of chloracetic acid, but as the displacements increase in number an increase occurs, so that the temperature difference of dichloracetic acid and trichloracetic acid is greater than that of acetic acid itself; this is most evident in the trichlorinated acid. In octylic chloride, the temperature difference is also evidently low.

With reference to bromine, octylic bromide gives a slightly higher number than the chloride, but it is still lower than that estimated for octane. Propylic bromide also gives a lower number than that estimated for propane, so that mono-displacements by these two halogens have a reducing influence on the temperature differences, that of chlorine being the most marked.

Iodine influences the temperature difference in an opposite direction to the other halogens, and increases it; this is especially seen to be the case in the di-displacement compound methylene diiodide, where it amounts to no less than 0·865.

In the aromatic series, similar kinds of differences exist; thus, in the mono-halogen derivatives of benzene, the temperature difference of chlorobenzene is the lowest of the three, being considerably below that of benzene; bromobenzene comes next, being only a little above chlorobenzene, but still a little less than that of benzene, whilst iodobenzene is the highest, and a good deal above that of the hydrocarbon.

The numbers obtained for phenylic sulphide evidently show that sulphur compounds have high temperature differences.

From the foregoing results it is seen that there is a close analogy between the temperature differences of corresponding compounds in the fatty and aromatic series, and there can be but little doubt that if the substance were subjected to a larger number of measurements, so as to yield results of still greater accuracy, that even closer agreements would be found to exist.

With reference to the percentage changes for the variation of 100° of temperature calculated on Sp. R./*d*, or on the molecular rotation, so far as they have been considered, they do not appear to give much useful information. It will be seen that they vary from −0·824 per cent. in chloracetic acid to −5·184 per cent. in ethyl α-naphthyl oxide (with the exception of water, which gives +0·8). In the benzene hydrocarbons, they gradually diminish as the hydrogen is displaced by methyl; this is what might be expected, as fatty compounds have smaller temperature differences than aromatic compounds. In halogen derivatives of benzene, it is also seen that the percentage increases from the chloro-derivative to the bromo-, and then more decidedly so to the iodo-derivative.

It is worth remarking that in most cases where the magnetic rotations are influenced by the constitution of substances, so that they give higher or lower "series constants," the same thing occurs in reference to the temperature differences. This is seen in the case of substances containing CO or CO·OH-groups, which have both lower series constants and temperature differences than the paraffins. In compounds containing halogens, there is also an analogy between the temperature differences and series constants, both changing in a similar manner, the numbers rising from the chlorine to the bromine, and then, but to a much greater extent, to the iodine compounds.

The unsaturated substances also give higher series constants and temperature differences than the saturated. The same analogy is found also in the case of displacement by NH_2 or $N(CH_3)_2$, as in aniline and dimethylaniline, also in α-naphthylamine.

There is, however, one exception to these analogies, and that is in the case of hydroxyl displacements. In magnetic rotations, the alcohols and phenols have higher series constants than their corresponding hydrocarbons, but their temperature differences are smaller; with this one exception, however, the analogy seems to hold good.

In some experiments on the refractive power of organic compounds at different temperatures (Trans., 1892, **61**, 307—310), it was shown that all the substances examined manifested a reduction of refractive power when heated, and it is also mentioned that the results are analogous in their relationships to those obtained in connection with magnetic rotations. This was stated to be the case more particularly in reference to the monhalogen derivatives of benzene, aniline, dimethylaniline, α-naphthylamine, and the unsaturated compounds ethylic cinnamate and cinnamic alcohol. Now that the temperature differences of the magnetic rotations are given, it will be seen how far this statement was justified.

On comparing the temperature differences of the refractive power and of the magnetic rotation of the halogen compounds above referred to, it is seen that they both rise from the chloro- to the bromo-, and then to a greater extent to the iodo-derivative. In the paper just referred to (*loc. cit.*, 309), it is stated that the difference found for bromobenzene was probably too small, and that most likely it should lie about midway between that of chlorobenzene and iodobenzene; the numbers given are, however, in all probability correct, for it will be noticed that the temperature difference of the rotation of this substance is in agreement with it, being considerably nearer the chloro- than the iodo-derivative.

With aniline and dimethylaniline, where there is such a remarkable increase in the temperature difference of the rotation, a similar result is found in the temperature difference of the refractive power; the same being true also in the case of α-naphthylamine.

Unsaturated compounds give equally comparable results. An exception is found in the case of water, which gives a very small temperature difference in relation to both properties, they however go in contrary directions, that of the magnetic rotation being a very small *plus* quantity, whilst that of the refractive power is a very small *minus* quantity; this exception may, however, eventually prove to be more apparent than real.

The analogies referred to above in respect to refraction, are only true if Gladstone's formula be used in calculating the results, whereas, if that of Lorentz be employed, slightly higher numbers are obtained for an increase of temperature, a result which would not be expected, and is at variance with the magnetic rotations, which are found to fall (except in the case of water), whether the numbers are treated relatively, as in this paper, or whether the absolute values are determined. Moreover, if the refractive indices be divided by density, or $(\mu - 1)/d$ be taken, the numbers are always found to become lower with rise of temperature; it, therefore, appears that Gladstone's formula agrees best with the general character of the results obtained in connection with both properties.

The specific and molecular refractions of liquid compounds in many cases fall 0·5 or 0·7 per cent. for a rise of temperature of 100°. Therefore for the difference of temperature between the boiling point of a substance and that of the atmosphere, it must in many cases amount to considerably more than this; we do not know, however, that this change ceases at the boiling point of the substance, or whether any further fall occurs during the transition from the liquid to the gaseous condition.

Owing to the existence of temperature differences, it is necessary, especially in the case of aromatic compounds, to compare them at one temperature; 15° has therefore been selected. It is not always possible, however, to make the measurements at this point, especially in hot weather, because when working below the atmospheric temperature the glass ends of the tubes become covered with moisture, and, moreover, it not unfrequently happens that substances have to be examined in the fused state. When the temperature difference is known, it is very easy to reduce the molecular rotation to 15°; when unknown, the only way is to apply the temperature difference of the most nearly allied substance. As the corrections of this kind, in the majority of cases, are only for a very few degrees, this is sufficiently accurate for all practical purposes, but, in other cases, where large variations occur, it is not so satisfactory, although it is not likely to lead to any important errors.

With reference to the rotation of water. To say that the rotation of this liquid with rising temperatures, does not fall quite to the same extent as its density, is the same as saying that its rotation increases with temperature. This is an interesting, though anomalous result, already referred to, no other substance yet examined behaving in this manner. It has been shown in previous papers, that when chemical combination takes place between two substances, the rotation of the product is not equal to that of the sum of their rotations, but somewhat less; therefore, if a substance were dissociated by heat the rotation would increase. This result would then be analogous to that which happens in the case of water, although probably the influence on the rotation would be much larger. In the case of water, however, it is not assumed that any chemical change takes place, but it is generally believed that water consists of molecular complexes, which when heated become simplified, and if this be so, the magnetic rotation may be affected in a manner similar to that caused by chemical dissociation, though probably to a small extent only; this would furnish an explanation of the anomalous rotation of this liquid. The question as to whether this, if correct, would influence the rotation to the extent of 0·8 per cent. only for 100°, by which it differs from the density, it is impossible to decide, although the probability is that it would be rather more; because if water, independently of this, behaves like other substances, it will have a temperature difference, though probably a low one, and this acting in a direction opposite to that due to the breaking down of molecular complexes, would make this influence appear smaller than it really is.

In a previous paper (Trans., 1894, **65**, 404),* it was stated that it did not appear probable from the results of the measurements of the rotations of acetic and propionic acids at different temperatures, that these rotations were influenced by simple molecular changes, because both acids gave nearly similar results at high temperatures, notwithstanding they are supposed to differ considerably in molecular complexity. Acetic acid, however, is known to be dissimilar in its physical properties from propionic acid, and it is possible that its temperature difference may be larger than that of propionic acid, more so, in fact, than is indicated by experiment; for if molecular simplification takes place, it would operate in the opposite direction, and would make the temperature difference appear smaller than it is, that these results do not really give any definite information on this subject. The anomalous rotation of water, however, renders it probable that the simplification of molecular complexes does cause a small rise in magnetic rotations. If this be so, a few of the examples already given of temperature differences in the foregoing tables may really be larger than they appear to be. Attention has already been drawn to the small temperature differences of the alcohols and phenols, and it will be remembered that Ramsay and Shields regard the former as compounds of molecular complexity.

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* In this paper, the mistake was made of inferring that the breaking down of molecular complexes would be likely to cause reduction in rotation.

SECTION II.—CONSIDERATIONS RESPECTING THE ROTATION OF AROMATIC COMPOUNDS.

In considering the rotations of the aromatic compounds, it will perhaps be most convenient first to deal chiefly with those relating to substances containing the group C_6H_6 as these, in most cases, represent fatty compounds with hydrogen displaced by this radicle; moreover, in substances of this nature the subject of position in the benzene nucleus does not arise. With these, however, as well as with those in which position has to be considered, the interpretation of the results are complex, because it is found that most of the compounds containing benzenoïd and paraffinoïd residues do not give rotations which are the mean of their separate rotations, but that the influence of some of the groups, if in direct union with the nucleus or very closely associated with it, causes an augmentation of the rotation of the products to a greater extent than would be expected from their composition, whilst others produce an opposite effect. This is not only the case with groups containing carbon, but also with those containing nitrogen or some of the halogens. This peculiar influence, due to the association of the nucleus with other groups, is also often prevented or screened off as it were, more or less, by intervening groups, such as carbonyl, as will be seen when considering the results which have been obtained.

Ethereal Salts of Benzoic acid.

The following table shows the molecular rotation of those ethereal salts of benzoic acid which have been examined, together with the observed differences for the variation in composition by CH_2, and for the *iso*-group.

The average of all the differences for CH_2 is 1·055, or, excluding the first, as it has reference to a methylic salt, it is 1·037, or a trifle more than the ordinary value of CH_2 in the fatty series, namely, 1·023.

An interesting point is noticed when considering this table, namely, that benzoic acid, $C_6H_5{\cdot}COOH$, appears to be more correctly represented as acetic acid, $CH_3\cdot COOH$, in which the methyl is replaced by phenyl, than as phenylformic acid.

Substance.	Mol. rot. 15°.	Diff. for CH_2.	Diff. for iso- group.
Methylic benzoate	12·743		
		1·111	
Ethylic benzoate	13·854		
		1·022	
Propylic benzoate	14·873		
		—	0·077
Isopropylic benzoate	14·950	1·079	
Butylic benzoate	15·952		
		—	0·096
Isobutylic benzoate	16·048	4)4·040	
		1·010	
Octylic benzoate	19·992		

It may be seen from the above table that the differences between methylic, ethylic, and propylic benzoates are 1·100 and 1·019 respectively, corresponding more nearly with those between methylic, ethylic, and propylic acetates than with those found in the case of the formates, as the following table shows.

Substance.	Mol. rot.	Diff.
Methylic formate	2·495	
		1·069
Ethylic formate	3·564	
		0·970
Propylic formate	4·534	
Methylic acetate	3·362	
		1·100
Ethylic acetate	4·462	
		1·025
Propylic acetate	5·487	

Of the differences, for CH_2, that between propylic and butylic benzoate is rather larger than what might have been expected; this may possibly be due to a slight impurity, since the normal butylic alcohol used in its preparation, although repeatedly fractionated, did not boil as constantly as could have been wished. If, however, an average of all the differences be taken, omitting the first, 1·037 is obtained as already noticed (or if that between propylic and ethylic benzoate be taken 1·025 is obtained), so that in these benzoates it appears that the alcohol radicles have very nearly the same values as in the ethereal salts of the fatty acids.

This is interesting because it shows that the oxygenated group, –CO·O–, which links these radicles to the phenyl, screens them almost perfectly from its influence, otherwise their apparent values would be greater, as will be seen further on.

The boiling points of the ethereal salts of benzoic acid differ from each other to a smaller extent than those of the fatty acids, which amount to about 22°, thus

Substance.	B. p.	Diff. for CH_2.	Iso-group.
Methylic benzoate	198·6°	13·2°	
Ethylic benzoate....................	211·8	18·9	
Propylic benzoate	230·7	—	12·2°
Isopropylic benzoate	218·5	18·3	
Butylic benzoate....................	249·0	—	7·5
Isobutylic benzoate.................	241·5		

The following table gives the differences in the densities for each CH_2.

Substance.	d 15°/15°.	Diff. for CH_2.	Diff. for iso- group.
Methylic benzoate	1·0942	0·0419	
Ethylic benzoate....................	1·0523	0·0247	
Propylic benzoate	1·0276	—	0·0104
Isopropylic benzoate	1·0172	0·0165	
Butylic benzoate....................	1·0111	—	0·0076
Isobutylic benzoate.................	1·0035	4)0·0432	
Octylic benzoate....................	0·9679	0·0108	

The isopropylic and isobutylic salts show the characteristic differences from the normal nearly as strongly as in the fatty series.

The results tabulated above, relating to the three properties—molecular rotation, boiling point, and density—are clearly seen if graphically represented as in Fig. 17, where it will be observed that the values for the boiling points and densities are included in a regular curve, with the exception of those for methylic benzoate as shown by the dotted lines. In the case of the rotations, which are represented by the sum of the numbers of the abscissæ and ordinates referring to them, the numbers do not form a regular curve, but from the large difference between the rotation of methylic and

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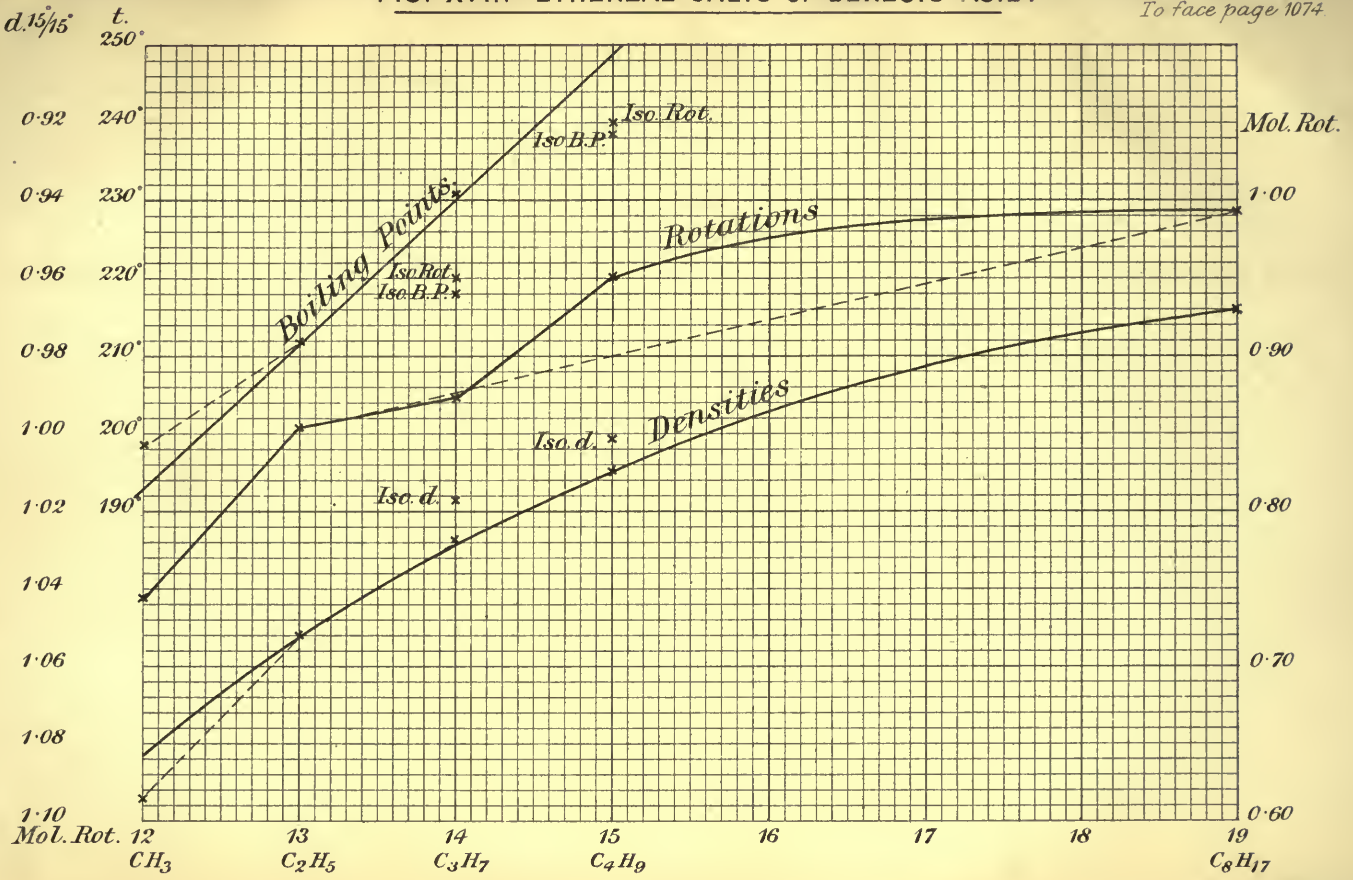
FIG. XVII. ETHEREAL SALTS OF BENZOIC ACID.



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ethylic benzoates, the former evidently behaves abnormally, as in the case of the boiling point and densities. The irregularity between ethylic, propylic, and butylic benzoates would not have been expected because they are not found in the case of the acetates, but whether this is real or due to a slight impurity in the butylic benzoate, as previously noticed, further experiment must decide. A difference of about 0·050 in the molecular rotation would cause this discrepancy. The rotations are more sensitive to slight impurities than the boiling points and densities.

If these compounds behaved like the acetates, the rotation would follow the dotted line between ethylic and octylic benzoates.

Phenylic Salts of the Fatty Acids.

It is difficult to prepare these substances in a pure state, phenylic propionate, for example, was at first obtained as an oil, but afterwards in a crystalline condition, and although but little difference was found in the densities and boiling points of the two products, yet the rotation of the crystalline specimen was slightly lower than that of the oil, indicating that the latter probably contained a little phenol. It is possible also that the specimens of phenylic acetate and phenylic butyrate examined may have contained a trace of the same impurity, as neither of them could be obtained in a solid condition, and they are, moreover, easily acted on by alkali; it was not possible, therefore, to be certain that the phenol was entirely removed. The phenylic œnanthate used was probably quite free from phenol, because it can be thoroughly washed with dilute potash without decomposition; its boiling point (282·3°), moreover, is so very much higher than that of phenol (182·6°).

Four of these phenylic salts were examined, yielding the numbers given in the following table.

Substance.	Mol. rot.	Diff. for CH_2.
Phenylic acetate..........	12·953	0·720
Phenylic propionate	13·673	1·088
Phenylic butyrate........	14·761	3)3·162
Phenylic œnanthate	17·923	1·054

These differences show that there is a much smaller variation for the CH_2 between the acetate and the propionate than between the other compounds; this is again analogous to the results obtained in the fatty series, the difference between ethylic acetate and propionate being 0·990, whereas in the case of the higher members of the series it amounts to 1·023; in the above phenylic compounds the average difference for CH_2, excluding that of the acetate as not strictly comparable, is higher than the latter number, being 1·062.

In the phenylic salts, the group linking the phenol to the alcohol radicle is the same as in the ethereal salts of benzoic acid, namely, –CO·O–, the difference between the two series being that the positions are reversed; in the first, the phenyl is associated with the oxygen, and the radicle with the carbonyl, whereas the opposite is the case with the benzoates. It would have been expected that this arrangement would have given the same difference for the change of composition by CH_2, but from the results it appears that the phenyl and fatty groups in this position exert some very slight influence on each other, which they do not in the benzoates.

The boiling points of this series of compounds show the following differences.

Substance.	B. p.	Diff. for CH_2.
Phenylic acetate..........	196·7°	14·3°
Phenylic propionate	211·0	16·5
Phenylic butyrate	227·5	3)54·8
Phenylic œnanthate	282·3	18·2

The densities at 15°/15° give

Substance.	Density 15°.	Diff. for CH_2.
Phenylic acetate..........	1·0809	0·0267
Phenylic propionate	1·0542	0·0275
Phenylic butyrate	1·0267	2)0·0448
Phenylic œnanthate	0·9819	0·0224

In Fig. 18 these tabulated results are represented graphically; the rotations, it will be seen, show a very striking difference in the case of phenylic acetate, the line connecting this with phenylic propionate going in an opposite direction to that which connects the other rotations. The latter is a fairly regular curve. The boiling points are included in a very slightly curved line, except that of phenylic acetate, as shown by the dotted line. The densities are also included in a regular curve, again with the exception of phenylic acetate. It is thus once more seen that in the case of phenylic acetate these three properties point out a difference between it and the other members of the series, the most striking variation noticeable being again that in relation to the rotation.

Comparison of the Ethylic Salts of Benzoic, Phenylacetic, and Phenylpropionic acids.

In this short series, the ethereal salts of the last two acids are isomeric with some of the ethereal salts of benzoic acid previously considered, where the difference of composition is in the acid itself,

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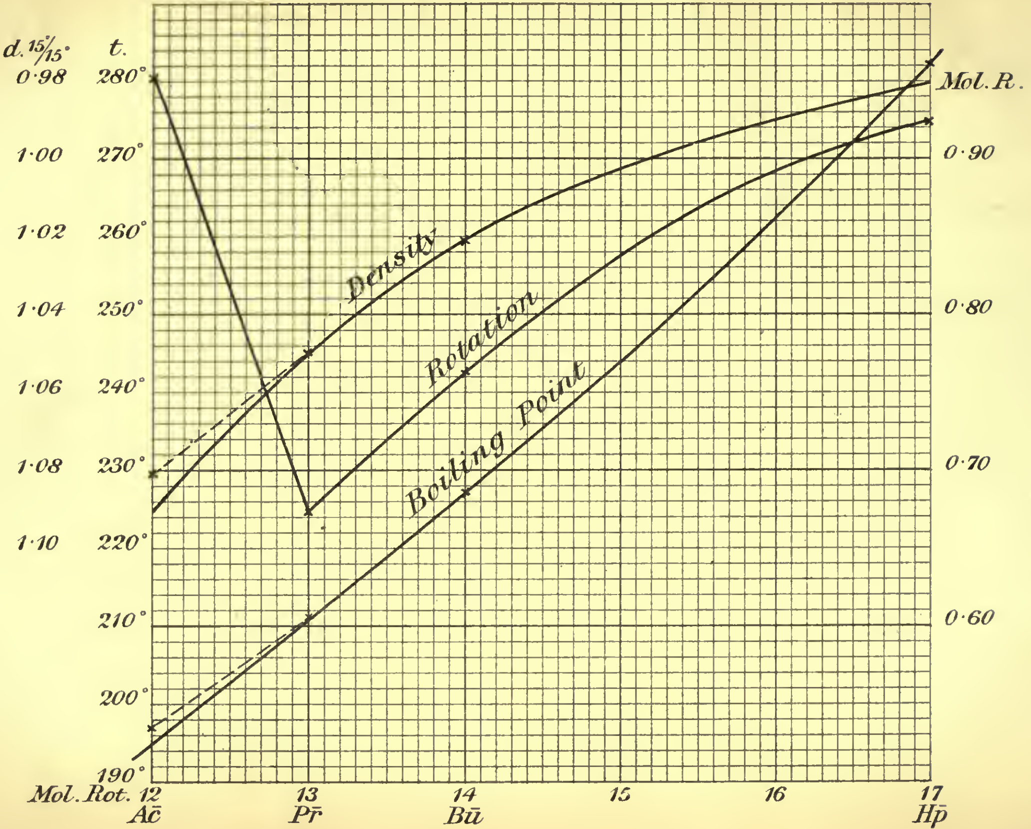
FIG. XVIII. PHENYLIC SALTS OF THE FATTY ACIDS.



instead of in the alcohol radicle of the salt. The following are the compounds which were examined, with their rotations, &c.

Substance.	Mol. rot.	Diff. for CH_2.
Ethylic benzoate	13·854	1·128
Ethylic phenylacetate	14·982	1·187
Ethylic phenylpropionate....	16·169	
Average..........		1·157

These compounds, as previously noticed, probably represent ethylic acetate, propionate, and butyrate, in which CH_3 is displaced by C_6H_5, and the differences are consistent with this, the first being the smaller of the two; in the above cases, however, they are both considerably larger than in the fatty series referred to, and this is apparently due to the CH_2 group in the last two compounds being in direct union with the phenyl, the rotation of the compound being increased thereby, in ethylic phenylacetate, however, this effect is apparently neutralised in part by the reducing influence of the COOEt group, with which it is also connected, otherwise it should have given the larger difference of the two.

The following is a comparison of the boiling points of these ethereal salts.

Substance.	B. p.	Diff. for CH_2.
Ethylic benzoate	211·8°	15·5°
Ethylic phenylacetate	227·3	19·9
Ethylic phenylpropionate....	247·2	

The relative densities also show considerable variations.

Substance.	d 15°/15°.	Diff. for CH_2.
Ethylic benzoate	1·0523	0·0061
Ethylic phenylacetate	1·0462	0·0250
Ethylic phenylpropionate....	1·0212	

From the results given in the three foregoing tables, it is seen that considerable variations again occur between the differences of the first and second members of the series.

Members of three isomeric series of compounds having been considered, it will be of interest to compare them. All the products, however, are not suitable for this purpose, such as the first members of the series, which always behave in a different manner from the others; for example, ethylic phenylacetate and methylic benzoate cannot be compared, for reasons which have already been explained, and, in fact, it is doubtful whether ethylic salts should be compared with those containing propyl and other higher radicles; any error such a procedure may cause will, however, be but small.

Substance.	Mol. rot.	Diff.
Phenylic propionate	13·673	0·181
Ethylic benzoate	13·854	
Phenylic butyrate............	14·761	0·112
Propylic benzoate	14·873	
Phenylic œnanthate	17·923	0·032
Heptylic benzoate (calc.) ...... = Octylic benzoate −1·037 × 2	17·955	
Propylic benzoate	14·873	0·109
Ethylic phenylacetate	14·982	
Butylic benzoate	15·952	0·217
Ethylic phenylpropionate......	16·169	

From the above, it is seen that the rotations of the phenol salts are a little lower than those of the benzoates; the rotations, however, gradually approach each other as the members of the series rise; this is due to the values for each change in composition by CH_2, not being the same in both cases, but slightly larger in the phenylic salts. In the next examples, it will be seen that the rotations of the benzoates are a little lower than those of the ethylic salts of phenylacetic and phenylpropionic acids, the divergence increasing with the higher member of the series. This is quite consistent, because the increase of the rotation for each CH_2 in the latter compounds is larger than in the benzoates.

Values for phenyl displacing hydrogen in the foregoing three series of compounds may be obtained by subtracting from their molecular rotations those of the corresponding fatty compounds, thus

Substance.	Mol. rot.	Diff. for C_6H_5, disp. H.
Propylic benzoate	14·873	10·409
Propylic acetate less CH_2 (5·487—1·023)	4·464	
Ethylic phenylpropionate	16·169	10·717
Ethylic propionate	5·452	
Phenylic propionate	13·673	10·332
Methylic propionate less CH_2 (4·364—1·023)............................	3·341	
Phenylic œnanthate.............	17·923	10·371
Œnanthylic acid	7·552	
Average		10·457

Some of these values are again referred to (p. 1092).

Influence of Etherification on Rotation.

α-Toluic or Phenylacetic Acid.

The aromatic acids being solids and most of them fusing at temperatures too high for rotation determinations, no attempt was made to examine a series of these acids ; it was, however, desirable to determine the rotation of one of them, and especially to compare it with its ethereal salt, in order to see what the influence of etherification was in the case of the aromatic acids. For this purpose, phenylacetic acid was employed, on account of its being easily soluble in ethylic benzoate, a convenient liquid to determine its rotation in, and unlikely to influence it chemically ; the specific rotation of this solvent, also, differs but little from that of the acid.

The following is a comparison of the rotation of the acid with that of its ethereal salt.

Mol. rotation of ethylic phenylacetate....	14·982
,, phenylacetic acid	12·743
C_2H_5 disp. H	2·239

This change in rotation for etherification is larger than that in the fatty series ; for example, in the case of propionic acid, with which this is, perhaps, most nearly comparable, it amounts to 2·000, so that in the aromatic series it is about 12·5 per cent. larger than in the fatty series.

By comparing the rotation of this acid with that of ethylbenzene, the effect of the carboxyl group when displacing methyl in the latter will be seen, the substances being thus related.

$C_6H_5{\cdot}CH_2{\cdot}CH_3$ and $C_6H_5{\cdot}CH_2{\cdot}COOH$.

Mol. rotation of ethylbenzene	13·414
,, phenylacetic acid....	12·743
Diff. for COOH disp. CH_3..	0·671

From this it is evident that the carboxyl group when displacing methyl reduces the rotation considerably. In the fatty series, there is also a reduction, but it only amounts to about one-sixth of the above (the rotation of heptane minus that of œnanthylic acid gives 0·117) ; this want of agreement may be due to the influence of the phenyl, which is only partially screened off by the CH_2 group in union with it, thus affecting the methyl in the hydrocarbon, although it would not influence the COOH group in the acid.

A value may be obtained for the phenyl in this acid by subtracting the rotation of acetic acid from its rotation; this gives 10·218, but if that of propionic acid, minus the value of CH_2, be employed, it is 10·309, which, probably, is the more accurate of the two.

Mixed Oxides containing Phenyl and Alcohol Radicles.

The following table gives a list of the substances examined and the results obtained.

Substance.	Mol. rot.	Diff for CH_2.
Phenyl methyl oxide........	13·958	1·171
Phenyl ethyl oxide	15·129	1·058
Phenyl propyl oxide........	16·187	
Phenyl isopropyl oxide	16·201	5)5·259
Phenyl isobutyl oxide	17·332	1·052
Phenyl octyl oxide	21·446	

The average value for CH_2 between the propyl and octyl compounds is 1·052.

In the first comparison between the methyl and ethyl compounds, the difference is larger than in the succeeding ones. No series of fatty oxides has been examined with which the foregoing can be compared, but if the alcohols which are closely related to these compounds be employed for this purpose, a certain analogy in the difference is found.

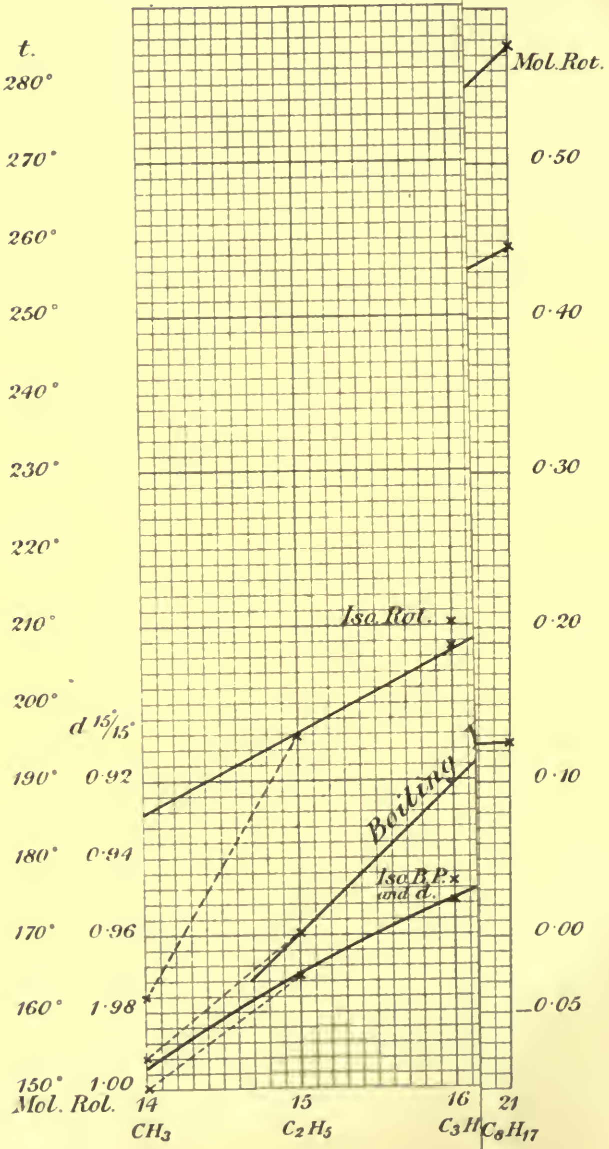
Substance.	Mol. rot.	Diff. for CH_2.
Methylic alcohol	1·640	1·140
Ethylic alcohol..............	2·780	0·988
Propylic alcohol	3·768	5)5·112
Octylic alcohol..............	8·880	1·022

From this table it is seen that a considerably larger difference exists between the two first members of this series than in the succeeding cases, just as there is between the two first mixed oxides.

It is curious that the isopropyl and propyl derivatives yield the same numbers, because iso-compounds usually give higher results than normal compounds. Their densities are also equal, so that if it were not that their boiling points differed, it might be thought that the iso-compound had changed over to the normal during its preparation. If, however, a comparison be made between the propyl and isobutyl compounds, a difference of 1·145 is found to exist; this is 0·093 higher than the average difference for CH_2, namely, 1·052, so that in this instance the iso-group exerts its ordinary influence by raising the rotation.

The boiling points of this series of compounds are as follows.

FIG. XIX. MIXED OX



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Substance.	B. p.	Diff for CH_2.	Iso-group.
Phenyl methyl oxide	153·9°	16·4°	—
Phenyl ethyl oxide..................	170·3	19·0	—
Phenyl propyl oxide..................	189·3		12·0°
Phenyl isopropyl oxide	177·3	5)95·9	
Phenyl isobutyl oxide	199·9	19·2	8·6
Phenyl octyl oxide	285·2		—

The relative densities are as follows.

Substance.	d 15°/15°.	Diff. for CH_2.	Diff. for iso-group.
Phenyl methyl oxide	0·9988	0·0286	—
Phenyl ethyl oxide..................	0·9702	0·0172	—
Phenyl propyl oxide	0·9530		−0·0066
Phenyl isopropyl oxide	0·9464	5)0·0393	
Phenyl isobutyl oxide	0·9331	0·0079	—
Phenyl octyl oxide	0·9137		—

In Fig. 19 the results given in the three foregoing tables are represented graphically, and it will be seen, as in the previous cases, that when a variation occurs in the rotations, a corresponding variation is usually found in the boiling points and densities.

Hydrocarbons containing Phenyl.

The following table contains a list of the substances examined which contain one phenyl group, and also the results obtained in their investigation.

The first difference in this table is an exceptional one, and not comparable with the others, as it is due to the introduction of a fatty group into the benzene ring; this interferes with its symmetry, and may slightly influence the rotation of the nucleus itself; moreover, displacement of hydrogen by methyl, except when iso-compounds are formed, often influences the rotation to a smaller extent than is caused by the addition of a CH_2 group.

Substance.	Mol. rot.	Diff. for CH_2.	Diff. for iso-group.
Benzene	11·284	0·873	—
Toluene	12·157	1·257	—
Ethylbenzene	13·414	1·139	—
Propylbenzene	14·553	—	0·080
Isopropylbenzene (cumene)	14·633		
Isobutylbenzene	15·615	—	—

On examining the constitution of ethylbenzene and propylbenzene, it is seen how the different groups are related in these substances.

$C_6H_6 \mid CH_2 \mid CH_3$ Ethylbenzene.

$C_6H_5 \mid CH_2 \mid CH_2 \mid CH_3$ Propylbenzene.

Taking toluene as the initial product from which to consider the other differences, it is seen from the above table that the first introduction of CH_2 in direct union with the nucleus, influences the rotation to a larger extent than the second.

In the rotation of cumene, the existence of the iso-group is clearly indicated, the value obtained being higher than it is in propylbenzene, thus confirming the recent work on cumene, showing that it contains the isopropyl group. Isobutylbenzene does not appear, at first sight, to show the existence of this group, but this may be due to the phenyl and methyl groups not exerting so great an influence on each other, on account of their being further apart; the examination of butylbenzene would show if this were so. It would also be desirable to re-examine isobutylbenzene prepared by the hydrolysis of a salt of one of its sulphonic acids, as the purity of these compounds prepared by ordinary methods appears to become more doubtful as the size of the paraffinoïd group increases.

In the following table, the boiling points and densities of these hydrocarbons are given with their differences.

Both in the boiling points and the densities, there are marked irregularities in this series, and the same is the case in the magnetic rotations.

In Fig. 20, the results contained in the foregoing tables are plotted out, and show the somewhat striking differences found in connection with the three properties to which they relate. From this it is seen that the line connecting the rotation of benzene with that of toluene is in the opposite direction to that connecting the rotations of the

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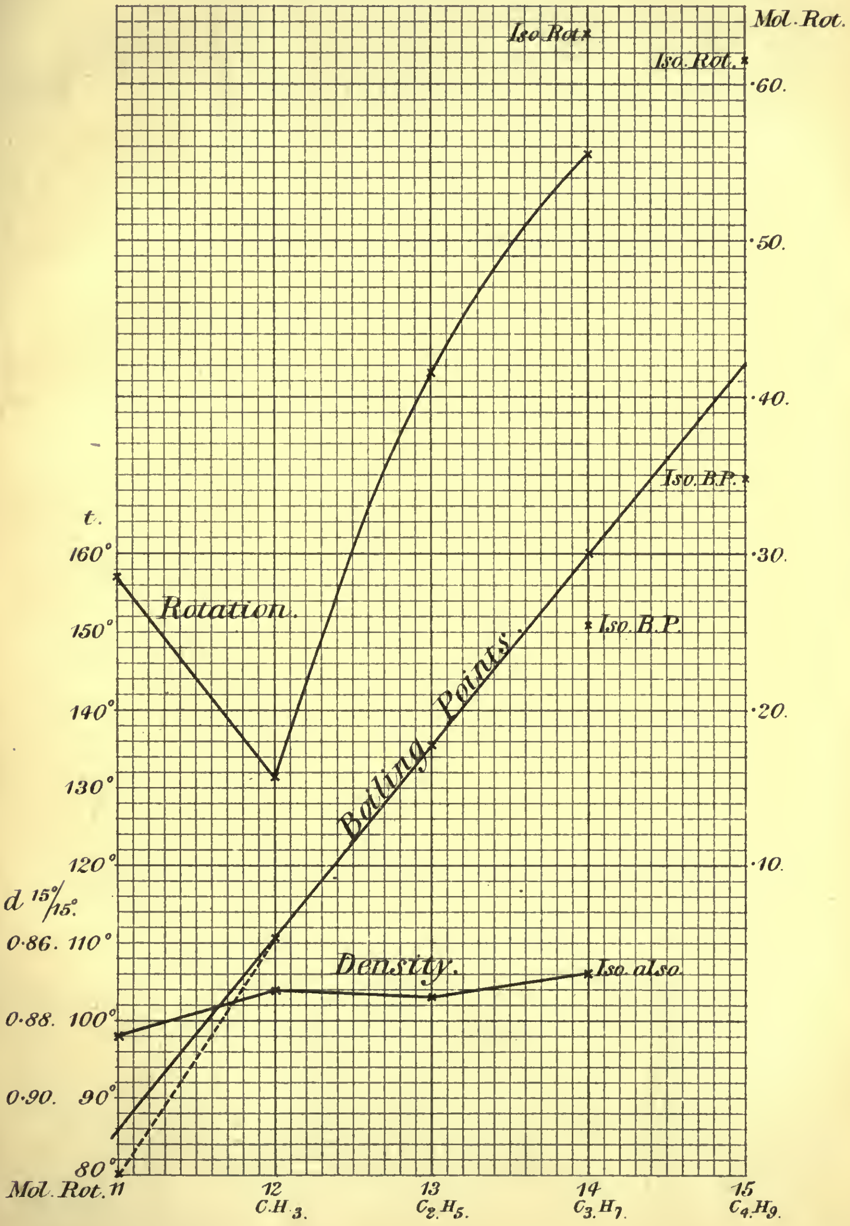
FIG. XX. HYDROCARBONS CONTAINING PHENYL.



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next two hydrocarbons. The direction the line between ethylbenzene and propylbenzene takes also increases in curvature, and probably would do so much more rapidly for butylbenzene, which should have a lower rotation than the isobutyl compound.

Substance.	B. p.	Diff. for CH_2.	d 15°/15°.	Diff. for CH_2.
Benzene	80·3°		0·8853	
		30·3°		−0·0130
Toluene	110·6		0·8723	
		24·9		+0·0007
Ethylbenzene	135·5		0·8730	
		23·7		−0·0062
Propylbenzene	159·2		0·8668	
Isopropylbenzene	152·9		0·8668	
		16·3		−0·0046
Isobutylbenzene	169·2		0·8714	

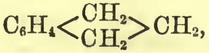
The boiling points of the three highest hydrocarbons are practically included in a straight line, but that of benzene is situated some distance from this, as shown by the dotted line. The densities, however, are the most striking, especially on comparing those of toluene and ethylbenzene, where the connecting line between them takes a slightly downward direction, instead of being upward as in the other instances. It is remarkable that the densities and expansions of normal and isopropylbenzene should be identical.

That the boiling point of isopropylbenzene is lower than that of the normal compound is what might have been expected, and that benzene should differ considerably in its physical properties from the other hydrocarbons of the series is not remarkable, because, unlike them, it does not contain any paraffinoïd group.

By dividing the molecular rotation of benzene by six, a value, 1·880, is obtained for CH; this is very much in excess of that found in the paraffins (0·769).

Hydrindene (*Synthetical*).

This hydrocarbon, which is a trimethylenebenzene,



$$C_6H_4{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}CH_2,$$

has the same composition as allylbenzene, $C_6H_5{\cdot}CH{:}CH{\cdot}CH_3$, but in the first the addition to the benzene is made up of a closed chain of saturated groups, whilst in the second it consists of an unsaturated open chain. The difference between the rotations of these compounds is very striking.

Allylbenzene	17·599
Hydrindene	13·928
	3·671

showing how strongly magnetic rotations indicate such changes of constitution.

Hydrindene differs from propylbenzene in containing H_2 less. If, therefore, the value of this be deducted from the rotation of the latter, a comparison can be made, thus

Propylbenzene........	14·553
Less H_2..............	0·508
	14·045
Hydrindene	13·928
Difference......	0·117

The want of agreement is not so large considering the difference in structure of the two hydrocarbons, so that probably there is nothing abnormal in the rotation of this compound.

It will be of interest here to consider the rotation of benzene in relation to that of a saturated ring compound. From the numbers obtained from the substances of this nature discovered by W. H. Perkin, jun., the rotation of hexahydrobenzene would be about six times that of the usual value for CH_2 found in the fatty series, or $1·023 \times 6 = 6·138$.

Another and more trustworthy estimate may be obtained from the rotation of *cis*-hexahydro-orthotoluic acid, methylhexamethylenecarboxylic acid (obtained by P. C. Freer and W. H. Perkin, jun., Trans., 1888, **53**, 209), and orthotoluic acid; the difference between them should give that for the H_6 by which they differ, thus

Orthotoluic acid, estimated from the ethereal salt..	12·826
Hexahydro-orthotoluic acid	7·975
Difference for H_6.......................	4·851

This subtracted from benzene should then give a value for C_6H_{12}.

Benzene	11·284
Less difference for H_6..	4·851
C_6H_{12}..........	6·433

This is not far from the first rough estimate given.

As already pointed out (Trans., 1895, **67**, 263), the rotation of benzene is higher than that of dipropargyl by 0·845.

In the open chain hydrocarbons, the difference in rotation for the loss of H_2 increases each time it is repeated; thus, starting with hexane they are 0·827, 0·947, 0·955, and 1·045 respectively, and it is possible that something of the same kind will be found to exist between the different hydrobenzenes, though probably that between benzene and dihydrobenzene would be the largest, because, as it would be the first conversion of $-CH\colon CH-$ into $-CH_2{\cdot}CH_2-$, it would have the initial effect of destroying the uniformity of the ring formation.

The difference of rotation due to the unsaturation of hexahydrobenzene by loss of H_6 and consequent conversion into benzene, appears to give an increase of about 4·851. This is much greater than that in the open chain compounds, as shown by comparing hexylene and dipropargyl, where it amounts to only 2·962.

With respect to the value of phenyl in benzene, the data for its estimation are somewhat uncertain, because the value of hydrogen in the aromatic series is not known with certainty. If it has the ordinary value of 0·254, which is most probably the case, this when subtracted will give 11·030 as the value of C_6H_5; this, no doubt, will be very near the truth, and on again subtracting 0·254 (the value of H) from this, 10·776 will be obtained as representing C_6H_5 when displacing hydrogen. This is a higher value than in any of the foregoing oxygenated compounds, although near that in ethylic phenylpropionate, which is 10·717; this is interesting, because it shows that as the CH_2 groups accumulate between the nucleus and the carbonyl, the influence of the latter on the rotation diminishes, and the phenyl gradually attains the same influence that it has in benzene.

Mono-, Di-, and Tri-phenylmethanes, Dibenzyl and Diphenyl.

The rotation of phenylmethane, or toluene, has already been referred to, but it will have to be considered again in reference to the other members of this series.

In the following table, the list of these hydrocarbons is carried on to tetraphenylmethane, which is at present unknown, the rotation of this substance having been estimated by continuing the curve formed by the differences found for the other members of this series when C_6H_5 displaces hydrogen. This will probably give a moderately accurate idea of its rotation, and will be of interest for comparison sake. The rotation of methane has also had to be estimated, thus: $C = 515 + H_4, 1{\cdot}016 = 0{\cdot}254 = 1{\cdot}531$. This is, however, probably either a little higher or lower than the true value, as it is the first member of the series of paraffins; the error, however, is not likely to be large.

Substance.	Mol. rot.	Diff. for C_6H_5, disp. H.
Methane (calc.)	1·531	
Phenylmethane (toluene)	12·157	10·626
Diphenylmethane	23·845	11·688
Triphenylmethane	36·011	12·166
Tetraphenylmethane	48·258	12·247
C_6H_5 disp. H = Average		11·682

From this table it is seen that the difference increases considerably for each succeeding C_6H_5 as it displaces hydrogen in methane, assuming that the carbon and hydrogen of the methane residues remain of the usual value found in the paraffins; this, however, is improbable, because in ethylbenzene it is seen that the influence of CH_2 when in union with the nucleus increases the rotation by 1·257 instead of 1·023, or 0·234 more, and, therefore, if associated with two phenyls, as in diphenylmethane, it is probable that there would be twice this increase, or 0·468, making 1·491. These differences for C_6H_5 displacing hydrogen are evidently not quite accurate, being apparent only, and not real.

Dibenzyl or Diphenylethane.

This substance is of interest on account of its relationship to diphenylmethane, differing from it simply by containing two CH_2 groups instead of one, thus

$$\underbrace{C_6H_5{\cdot}CH_2{\cdot}C_6H_5}_{\text{Diphenylmethane.}} \qquad \underbrace{C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5}_{\text{Dibenzyl.}}$$

The relationship of their rotations is as follows

Molecular rotation of dibenzyl	24·977
,, ,, diphenylmethane ..	23 845
Diff. for CH_2..........	1·132

This is less than that found in the case of diphenylmethane, but is what might be expected, because in dibenzyl each phenyl is attached to a CH_2 group, whereas in diphenylmethane both phenyls are united to one CH_2 group, and, therefore, it is much more influenced by them; they are also not so far apart, and for this reason their influence is also likely to be greater. The apparent value of the CH_2 in dibenzyl will be about the average of that calculated from diphenylmethane and the above, namely, 1·491 and 1·132, or 1·311.

From the results obtained with the phenylmethanes and dibenzyl, it is seen that the value of phenyl increases as the number of molecules accumulate, evidently influencing each other, as well as the fatty groups associated with them.

Diphenyl.

This substance is an interesting example of the manner in which two phenyl groups influence each other when in direct union, thus

The molecular rotation of diphenyl is 25·304 ÷ 2 = 12·652; the latter number represents phenyl, and if from this the value of hydrogen in a fatty compound be taken, namely, 0·254, the number 12·398 is obtained as the value of this group when displacing hydrogen in a compound. This, it will be noticed, is larger than that found for phenyl in any compound where it is kept separate by intervening fatty groups.

A comparison with the most nearly related substance, diphenylmethane, will show this.

Molecular rotation of diphenyl	25·304
,, ,, diphenylmethane ..	23·845
Diff.	1·459

Thus it is seen that, notwithstanding diphenylmethane contains CH_2 more than diphenyl, its rotation is considerably the smaller of the two.

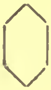
Diphenyl may be looked upon as benzene in which hydrogen is displaced by phenyl; when regarded from this point of view, we get

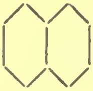
Molecular rotation of diphenyl	25·304
,, ,, benzene	11·284
C_6H_5 disp. H in benzene................	14·020

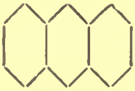
The largeness of this number shows that this method of calculating the value of phenyl in this compound is evidently incorrect, and that the numbers obtained for consecutive displacements found in this way for phenyl in diphenyl, or in such compounds as the phenylmethanes, must not be regarded as its actual value in such compounds, but the average must be taken; for it appears evident that in each of the compounds, diphenyl, diphenylmethane, and triphenylmethane, the phenyl groups must have equal values; thus, in diphenyl they will both be 12·652, in diphenylmethane 11·157, and in triphenylmethane each of them will be 11·493. This only refers, of course, to cases where the phenyl groups are similarly situated, but where the relationships of the groups are different from each other, as, for example, in such a compound as benzylaniline, the phenyl groups will have different values, so that it is evident that phenyl groups when directly united influence each other in such a way that the resultant product has a larger rotation than that of the two groups when separated.

Naphthalene, Phenanthrene, and Acenaphthene.

One of the points of interest connected with naphthalene and phenanthrene is their relationship to benzene, because they are constituted of two and three condensed nuclei, their starting point being the benzene nucleus itself. It would have been more satisfactory if the rotation of anthracene could have been also determined, but this hitherto has not been found possible, on account of its sparing solubility in all suitable solvents and its high fusing point, the relationship between this and naphthalene being strictly comparable with that between benzene and naphthalene; these three compounds being represented thus

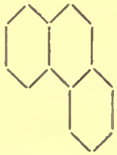






,

whereas phenanthrene is



,

and therefore is not quite so suitable for the purpose of comparison.

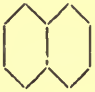
In the following table, the composition, rotation, and differences are given for the three hydrocarbons.

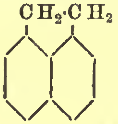
Substance.		Diff. in composition.	Mol. rot.	Diff. for C_4H_2.
Phenanthrene....	$C_{14}H_{10}$	C_4H_2	36·959	11·834
Naphthalene	$C_{10}H_8$	C_4H_2	25·125	13·841
Benzene	C_6H_6		11·284	

From this, it is seen that the addition of C_4H_2, or rather the displacement of H_2 by –CH:CH·CH:CH– (which, being two-thirds of benzene, has a rotation in that compound of 7·522), has, when introduced into the benzene nucleus so as to form naphthalene, caused the latter to have a rotation more than twice that of benzene itself. This rotation is also nearly as high as that of diphenyl (25·304), which contains two benzene nuclei, and therefore C_2H_2 more. The second introduction of –CH:CH·CH:CH–, so as to produce phenanthrene, again has a remarkably great influence, although not quite so large as the first; probably in anthracene it would be found to be quite as large, because usually the influence of these large aromatic groups increases as they are repeated.

The rotation of phenanthrene is even higher than that of triphenylmethane (36·011), although the latter contains three benzene nuclei, and also C_5H_6 more in its composition. This shows how much more the closer kind of association which exists in naphthalene and phenanthrene affects the rotation than the simple single union of benzene nuclei, either directly with one another or with the intervention of a saturated monocarbon group.

Acenaphthene differs from naphthalene by containing the double methylene group, $-CH_2·CH_2-$, displacing two hydrogens, one in each nucleus.





Their rotations are—

Molecular rotation of acenaphthene......	28·636
„ „ naphthalene	25·125
$-CH_2·CH_2-$ disp. H_2	2)3·511
	1·755

This difference for CH_2 displacing H shows that the influence of these groups, when united to naphthalene, is augmented more than in dibenzyl, where they are 2·622 instead of the ordinary amount of 2·046 found in the fatty series.

Acenaphthene is isomeric with diphenyl, but their rotations differ considerably; thus

Molecular rotation of acenaphthene......	28·636
„ „ diphenyl..........	25·304
Diff.	3·332

This is a very striking difference, and is a good example of the way magnetic rotations are influenced by variations in structure.

The consideration of the other hydrocarbons examined will be found further on, in connection with the subject of position, namely, that of cymene and indene, whilst that of cinnamene, allylbenzene, butenylbenzene, and stilbene are considered in connection with unsaturated compounds.

The Effect of Hydroxylic Displacement in Benzene and Toluene.

The displacement of an atom of hydrogen in benzene by hydroxyl has the effect of modifying its rotation in the same direction as a similar displacement affects the paraffins, namely, in increasing it, but in the present case the change is much greater, thus

Molecular rotation of phenol............	12·140
,, ,, benzene	11·284
Diff. for disp. of H by OH	0·856

In the paraffin series it is

Molecular rotation of heptylic alcohol	7·850
,, ,, heptane	7·669
Diff. for disp. of H by OH	0·181

When the hydroxylic hydrogen of phenol is displaced by methyl, a further large rise in rotation, considering the change in composition, takes place, thus

Molecular rotation of phenyl methyl oxide	13·958
,, ,, phenol............	12·140
Diff. for CH_3 disp. H...............	1·818

By displacing hydrogen in the methyl of toluene by hydroxyl, thus forming benzylic alcohol, a much smaller change of rotation occurs than in the case of the formation of phenol, thus

Molecular rotation of benzylic alcohol....	12·400
,, ,, toluene	12·157
Diff. for disp. of H by OH_2	0·243

By displacing the hydroxylic hydrogen in this alcohol, the following change in rotation takes place.

Molecular rotation of benzyl methyl oxide	13·417
,, ,, benzylic alcohol....	12·400
Diff. for disp. of H by CH_3	1·017

In the last two cases, the numbers closely correspond with those obtained in the paraffin series, being, in the case of the alcohol, only 0·062 higher, and, in the case of the oxide, about 0·10 higher.

The cause of this difference between phenol and benzylic alcohol illustrates what has already been referred to in connection with other compounds, in respect of the influence which phenyl and other groups have on the rotation, when in direct union, or separated by intervening groups. Thus, in the case of phenol, the direct union of the hydroxyl with the nucleus gives a rotation which is relatively a good deal higher than when a CH_2 group partially screens them from each other, as in benzylic alcohol. This difference in magnetic rotation between phenol and benzylic alcohol is also in agreement with the widely different chemical properties of the two substances.

The consideration of the rotations of the cresols and polyhydroxybenzenes will be found at p. 1127.

Effect of Carbonyl Displacements on Rotation.

Benzaldehyde, Acetophenone, Ethyl Phenyl Ketone, and Benzophenone.

These substances show the influence which $C{:}O$ displacing CH_2 has on the rotation of benzenoïd hydrocarbons.

Benzaldehyde gives a lower rotation than toluene, thus

Molecular rotation of toluene	12·157
,, ,, benzaldehyde......	11·864
	0·293

In the fatty series we get a similar, but slightly smaller, difference,

Molecular rotation of heptane	7·669
,, ,, œnanthaldehyde ..	7·422
	0·247

On comparing ethylbenzene with acetophenone, a similar difference is found, though somewhat larger, thus

Molecular rotation of ethylbenzene	13·414
,, ,, acetophenone......	12·597
	0·817

In the fatty series we get, in the case of a ketone, a somewhat smaller influence than in the case of aldehydes.

Molecular rotation of octane (calc.)......	8·692
,, ,, methyl hexyl ketone	8·519
	0·173

The rotation of ethyl phenyl ketone is very similar in character to that of acetophenone, as is seen on comparing it with propylbenzene, thus

Molecular rotation of propylbenzene	14·553
,, ,, ethyl phenyl ketone	13·635
	0·918

It is, however, a rather larger difference.

The following comparison is also of interest:—

Molecular rotation of ethyl phenyl ketone	13·635
,, ,, acetophenone......	12·597
Influence of CH_2........	1·038

This difference is very nearly the amount found for CH_2, in the series of ethereal salts of benzoic acid (1·037), and only a little above that found in the fatty series (1·023). From the relationship of the compounds, this is exactly what might be expected.

In the fatty series, when a C:O group displaces CH_2 in a paraffin, the ketone produced has a slightly higher value than the corresponding aldehyde, as seen above. The reverse occurs in the case of benzene hydrocarbons, that is to say, the ketones have a smaller value than the corresponding aldehydes. The reason of this is easily understood from the following considerations.

In ethylbenzene, the CH_2-group has been seen to have a relatively large influence on the rotation, on account of being directly attached to the nucleus; the methyl, which is only imperfectly screened from the latter, also acts in the same manner, although to a smaller degree. On the other hand, the C:O group in ketones, acetophenone for example, has apparently about the same value as in fatty compounds, and it also screens, in a marked manner, any radicles attached to it from the influence of the phenyl. Obviously, then, the high value of the CH_2 group, on becoming displaced by C:O, is lost, and that of the methyl group, also, is reduced, the ketone, as a consequence, having a value for the rotation a good deal lower than the hydrocarbon.

In toluene, the CH_3 group apparently has only a small value; therefore, on converting it into COH in the formation of benzaldehyde, the loss of rotation is not so great as in the formation of acetophenone from ethylbenzene.

With reference to the carbonyl in these compounds, this, instead of being increased in value by union with the phenyl, as the alcohol radicles are, actually has a reducing influence on the value of the phenyl itself; a few examples of the value of phenyl, deduced from compounds containing carbonyl in direct union with it, will show this. Some values obtained from such compounds have already been given, namely

Phenyl in propylic benzoate	10·409
,, phenylic propionate	10·321

The following are estimates for benzaldehyde and the two ketones.

Molecular rotation of benzaldehyde	11·864
,, ,, aldehyde − CH_2 (2·385 − 1·023)	1·362
Phenyl disp. H	10·502
Molecular rotation of acetophenone	12·597
,, ,, acetone − CH_2 (3·514 − 1·023)	2·491
Phenyl disp. H	10·106

Molecular rotation of ethyl phenyl ketone	13·635
,, ,, ethyl methyl ketone—CH_2 (4·433—1·023)...........................	3·410
Phenyl disp. H	10·225
Average	10·278

The highest value is that given by benzaldehyde, but all are evidently low when the average value is considered in relation to the value of C_6H_5 displacing H as found in benzene, namely, 10·776; it is evident, therefore, that carbonyl has a reducing influence on the rotation of phenyl when in union with it.

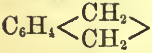
Benzophenone.—This ketone differs from those already considered, inasmuch as it is devoid of paraffinoïd groups, but contains two phenyl groups. As compared with its corresponding hydrocarbon, it is found to have a lower rotation, just as that of acetophenone is lower than that of ethylbenzene and propylbenzene, although the difference is not so large as in the case of the monophenyl ketones, thus

Molecular rotation of diphenylmethane ..	23·845
,, ,, benzophenone	23·371
Diff.	0·474

If the rotation of benzophenone is compared with that of diphenyl a considerable difference is found, thus

Molecular rotation of diphenyl..........	25·304
,, ,, benzophenone......	23·371
Diff..........	1·933

This is a very large amount, and due to two causes: Firstly, the separation of the two phenyls from each other, by the intervention of carbonyl, which prevents them from influencing each other as much as when they are directly united; this is also seen in the case of diphenylmethane. Secondly, the reducing action of carbonyl itself; this, however, is not so large as in the case of acetophenone, probably because it lies between the two powerfully rotating phenyl groups, which, being in such close proximity, overcome the screening influence of the CO group slightly, and influence each other.



Hydrindone.—This compound, which has the following structure, $C_6H_4{<}{CH_2 \atop CH_2}{>}CO$, may, perhaps, be referred to in connection with the ketones; when compared with hydrindene, its rotation shows—

Hydrindene	13·928
α-Hydrindone	13·768
Diff.	0·160

This difference is practically the same as that existing between a paraffin and a ketone, but much less than that between ethylbenzene and acetophenone, which is 0·817; the rotation therefore confirms the constitutional formula. The rotation is very similar to that of ethyl phenyl ketone, which contains H_2 less (13·635), showing that the fatty part of the compound is saturated, otherwise the rotation would be considerably higher.

Effect of the Carboxyl Displacements.

When the aromatic acids and their ethereal salts are compared with the benzene hydrocarbons containing the same number of carbon atoms, the influence of the carboxyl group becomes evident. The effect, however, is complex as in the case of the ketones.

The only acid which has been examined is phenylacetic acid; this may be compared with ethylbenzene, thus

	Mol. rot.	Reduction for disp. of CH_2 by $-COO-$.
Ethylbenzene	13·414	− 0·675
Phenylacetic acid	12·739	
Ethereal salts—		
Ethylbenzene	13·414	− 0·671
Methylic benzoate	12·743	
Propylbenzene	14·553	− 0·699
Ethylic benzoate........	13·854	
Average		0·682

The influence of this group, therefore, as might be expected, is very similar to that of carbonyl; this will be evident if the value of oxygen in the hydroxyl of acids, as found in the fatty series, and by which the rotation is increased (Trans., 1884, **45**, 573) be added to the above difference, thus 0·682 + 0·137 = 0·819, which is the same as that found on comparing ethylbenzene with acetophenone, but a little lower than that between propylbenzene and ethyl phenyl ketone. This is no doubt chiefly due to the discrepancy between the methylic and ethylic salts found on etherification of the acids; this amounts to 1·111 or about 0·074 more than the usual value for the difference for CH_2 in this series.

With reference to the influence of ethyl in the ethylic salts of the aromatic acids, see p. 1079.

Nitro-compounds.

Nitrobenzene.—The introduction of the NO_2-group in the place of hydrogen in benzene modifies the rotation in a remarkable manner, thus

Molecular rotation of benzene	11·284
,, ,, nitrobenzene ..	9·361
Reduction due to disp. of H by NO_2..	1·923

This group, therefore, instead of increasing the rotation by 0·229, the value of NO_2 when displacing hydrogen in the paraffin series, has actually reduced it by nearly 2·000; it is even less than the rotation of the open chain hydrocarbon dipropargyl (see Trans., 1889, **55**, 728).

The reducing influence of the NO_2-group has been already referred to in the case of chloropicrin, which has a lower rotation than chloroform by 0·175 (Trans., 1889, **55**, 347).

It will be convenient here to consider the other nitro-compounds which have been examined, as they are few in number, leaving the subject of position which is involved in them to be discussed further on.

Metadinitrobenzene.

The following shows the effect of introducing a second NO_2 group into benzene in the meta-position.

Molecular rotation of metadinitrobenzene..	9·647
,, ,, nitrobenzene	9·361
Increase	0·286

This second displacement has not further reduced the rotation of the compound, but increased it; so that it would appear that the first displacement acts in changing the type of the substance, after which further displacements have a more normal influence. It is difficult to estimate the value of the above increase, because the subject of position in dinitro-compounds is not known. The ortho-compound probably would have a higher rotation.

Ortho- and Para-nitrotoluenes.

The nitro-group, when displacing hydrogen in toluene, acts in an analogous way to what it does in benzene; thus

Molecular rotation of toluene	12·157
,, ,, paranitrotoluene...	10·214
Reduction............	1·943

Molecular rotation of toluene	12·157
,, ,, orthonitrotoluene ..	10·806
Reduction............	1·351

In both cases a considerable reduction in rotation occurs, that in the para-compound being similar to what it is in nitrobenzene. The difference in the variations between them is due to the influence of position.

Nitronaphthalene.

On comparing the rotation of this with the hydrocarbon it will be seen that a reduction occurs more than twice as large as that in nitrobenzene.

Molecular rotation of naphthalene.......	25·125
,, ,, α-nitronaphthalene ..	20·840
Reduction............	4·285

From the amount of this reduction, it would appear that both nuclei are effected by this displacement.

No other nitro-derivative of this hydrocarbon has been examined.

Nitriles.

In the fatty series, the rotations of the nitriles are lower than those of the corresponding hydrocarbons, thus

	Mol. rot.	Diff.
Propane, C_3H_8	3·577	0·246
Propionitrile, $C_2H_5{\cdot}CN$....	3·331	
Pentane, C_5H_{12}	5·638	2)0·502
Glutaronitrile, $C_3H_6(CN)_2$.	5·136	0·251

In both these cases the influence is very similar.

If the two nitriles be compared with the two ethereal salts of the acids they represent, they also show similar differences, thus

	Mol. rot.	Diff.
Ethylic propionate........	5·451	2·120
Propionitrile	3·331	
Ethylic glutarate	9·356	2)4·220
Glutaronitrile	5·136	2·110

There are two aromatic nitriles which have been examined, and with which similar comparisons to the above may be made, namely, benzonitrile and orthotoluonitrile. The latter being an ortho-compound will behave in nearly the same manner as a phenyl compound, in which position does not come into play (see p. 1134).

	Mol. rot.	Diff.
Toluene................	12·157	0·300
Benzonitrile	11·857	
Ethylbenzene	13·414	0·434
Orthotoluonitrile........	12·980	
Ethylic benzoate........	13·854	1·997
Benzonitrile............	11·857	
Ethylic orthotoluate	15·065	2·085
Orthotoluonitrile........	12·980	

It is seen from these comparisons that the differences are very similar to those in the fatty series, being a little larger on comparing them with the hydrocarbons, and a trifle lower when comparing them with the ethereal salts; this is probably due to the influence of the C_6H_5 group in the former being slightly higher than in the latter.

There is also another nitrile which has been examined, and would have been expected to give results even more like those of the fatty series than the foregoing, namely, benzylic cyanide; curiously, however, this is not the case, thus

	Mol. rot.	Diff.
Ethylbenzene	13·414	0·942
Benzylic cyanide........	12·472	
Ethylic phenylacetate....	14·982	2·510
Benzylic cyanide........	12·472	

In both these cases, the differences are considerably larger. It is true that benzyl compounds often give lower rotations than the corresponding toluene derivatives, but this varies with circumstances, and in the related ethereal salts of this series it is found that the rotations are nearly the same, thus

	Mol. rot.	Diff.
Ethylic orthotoluate	15·065	0·083
Ethylic phenylacetate....	14·982	

whereas in the corresponding nitriles, where an analogous difference might be expected, there is a considerable variation in the rotations of the compounds.

	Mol. rot.	Diff.
Orthotoluonitrile........	12·980	0·508
Benzylic cyanide........	12·472	

So that there appears to be something anomalous in benzylic cyanide.

In the naphthalene series, one comparison in respect to the α-nitrile may be made.

	Mol. rot.	Diff.
Ethylic α-naphthoate....	27·141	2·353
„ α-naphthonitrile.	24·788	

This difference is about 0·3 higher than in the case of ethylic orthotoluate and its nitrile, but in the naphthalene series the differences are usually larger than in the benzene series; this result, therefore, would indicate that the rotation of α-naphthonitrile is about normal.

It is remarkable that nitrogen, when in union with carbon as $-C{\vdots}N$, should behave in the manner it does, both in the fatty and aromatic series, having in both a considerably smaller influence than when in the form of NH_2 and united to carbon, this being especially seen in the aromatic series where its influence is so very great. When in union with carbon, as $\mathrm{N}<\begin{matrix}\mathrm{N}\\ |\\ \mathrm{N}\end{matrix}$, it is also found to have a large influence, as in azoimide, but it must be remembered that the chemical character of the cyanides is quite opposite to that of the amines.

Phenylazoimide, $C_6H_5N_3$.—The rotation of this substance can be compared with that of benzene, as it represents this hydrocarbon with hydrogen displaced by N_3, thus

Molecular rotation of phenylazoimide	14·769
,, ,, benzene	11·284
N_3 disp. H	3·485
Plus H	0·254
N_3..................................	3)3·739
N	1·246

The influence of nitrogen in the fatty series is only about 0·611, or in bases 0·717, so that it is evident that its influence in this kind of compound is to raise the rotation. In the case of aniline, as will be seen further on, the nitrogen united to the phenyl and hydrogen acts in the same manner, but to a very much greater extent, and it is very likely that in this compound the nitrogen directly attached to the phenyl may be the chief cause of this rise in rotation (see Phenylhydrazine). Assuming the other two to have the ordinary influence of 0·611, this one attached to the phenyl would have that of 2·253.

Monamines and their Derivatives.

Aniline and its Methyl, Ethyl, and other Derivatives.

It has already been shown that when nitrogen is directly united with phenyl, as in phenylazoimide, its influence causes the rotation to be high; this effect is, however, remarkably enhanced when the nitrogen is in union, not only with phenyl but also with hydrogen, as is the case in aniline; the following comparison will show this.

Molecular rotation of aniline	16·076
,, ,, benzene	11·284
Effect of NH_2 disp. H..............	4·792

This difference is nearly five times as great as in the paraffin series, where it is only 0·971. Taking this in another way, which assumes that the increase is in the C_6H_5 group, the following result is obtained.

Molecular rotation of aniline........	16·076
Less ammonia.....................	1·818
C_6H_5 disp. H......................	14·258

This gives an impossible number for phenyl, because even in diphenyl it only amounts to 12·658; it is evident, therefore, that this very large rotation must be due either to an enormously increased influence of the NH_2 alone, which also is unlikely, or else to its joint effect with that of the C_6H_5 group.

This remarkable rise due to the substitution of hydrogen by NH_2 is, however, greatly surpassed by the introduction of $N(CH_3)H$ and $N(CH_3)_2$ in its place, as is seen from the following table.

Substance.	Mol. rot.	Diff. for CH_3, disp. H.
Aniline............	16·076	
		3·548
Methylaniline......	19·624	
		3·264
Dimethylaniline....	22·888	

Now, in this instance, the increase for the change in composition caused by the displacement of one or two hydrogen atoms by methyl is considerably more than three times that ordinarily produced.

In the case of ethyl displacements, the following table shows the influence of this group when displacing hydrogen.

Substance.	Mol. rot.	Diff. for C_2H_5, disp. H.
Aniline............	16·076	
		4·491
Ethylaniline........	20·567	
		4·596
Diethylaniline......	25·163	

Here again a very large increase in rotation for the change in composition, due to the displacement of hydrogen by ethyl, is seen, amounting to more than twice the usual amount. It is of interest here to notice the different effects produced by methyl and ethyl on the rotations, because the latter are proportionally smaller than the former. The following comparisons show this.

1st diff. for C_2H_5......	4·491	0·943 diff. for CH_2.
,, ,, CH_3......	3·548	
2nd diff. for C_2H_5......	4·596	1·332 diff. for CH_2.
,, ,, CH_3......	3·264	
Average......	1·137	

These results show that the mono-carbon group directly united to the nitrogen, influences the rotation to a much larger extent than that indirectly attached, for the second carbon group in ethyl averages in these examples not very much more than that usually found for CH_2

when displacing H. This suggests, again, that this effect is caused by its being partially screened off, by the first carbon group, from the direct influence of the phenyl and nitrogen.

To better realise the enormous increase that takes place in the rotation when the hydrogen of benzene is displaced by $N(CH_3)_2$ or $N(C_2H_5)_2$, the following comparisons have been made.

Molecular rotation of dimethylaniline....	22·888
,, ,, benzene	11·284
$N(CH_3)_2$ disp. H..............	11·604

This difference, calculated from the probable rotation of dimethylamine, would be only about 3·108, whereas the above is nearly four times that amount.

Molecular rotation of diethylaniline	25·163
,, ,, benzene..........	11·284
$N(C_2H_5)_2$ disp. H	13·879

This difference, if calculated from diethylamine, would be only about 5·154, whereas it is nearly three times the amount.

Before considering any other derivatives of aniline, it will be as well to compare the differences existing between the methyl- and ethyl-anilines with those found in the case of fatty amines. As the methylamines have not been measured, the comparisons in the latter case must be made between the ethyl- and propyl-amines (Trans., 1889, **55**, 729—730).

Substance.	Mol. rot.	Diff. for CH_2.
Ethylaniline............	20·567	0·943
Methylaniline	19·624	
Diethylaniline..........	25·163	2)2·275
Dimethylaniline	22·888	1·137
Dipropylamine	7·549	2)1·887
Diethylamine	5·662	0·943
Tripropylamine	11·664	3)3·146
Triethylamine..........	8·518	1·049

In both the aromatic and fatty series, a similar kind of progression exists, the second differences being larger than the first, and it is again seen that the largeness of the rotation of the ethylanilines is not due to the second carbon groups, but to the first, which are in direct union with the nitrogen as in the methylanilines. This relation might have been even closer, if the strictly correct comparisons above referred to could have been made. All these differences refer to the

CH_2 not in direct union with the nitrogen, and it is seen how close the analogy is which exists between them.

The results obtained with *methyldiphenylamine* are of considerable interest. The rotation of this compound is very high indeed, but this might have been anticipated, because, if the rotation of aniline be considerably increased beyond the amount calculated for change of composition by the displacement of its hydrogen by methyl, it is only to be expected that a similar, but larger, effect would result from a displacement by phenyl.

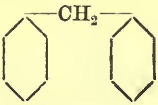
It will be best to compare this substance with methylaniline, thus

Molecular rotation of methyldiphenylamine ..	34·878
,, ,, methylaniline..........	19·624
Effect of C_6H_5 disp. H	15·254

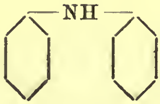
From this it will be seen that the introduction of phenyl increases the rotation by no less than 15·254, which, as in the case of methyl in methylaniline, is much above its usual influence, that of phenyl displacing hydrogen as estimated from benzene being only 10·746, or even in diphenyl 12·398.

From these results, it is evident that the differences shown in the tables connected with aniline and its derivatives are not real values for CH_2, &c., but show the influence of the introduction of the various groups on the rotation of the products as a whole. The results are very remarkable and striking.

When considering the rotation of the phenylmethanes, it was observed that the monocarbon group they contain, as in many other cases, screens off the phenyl groups, to some extent, from the influence they have on each other if united, it being shown that diphenyl has a larger rotation than diphenylmethane, notwithstanding the latter contains CH_2 more than the former. It is, therefore, interesting to see how the nitrogen group NH behaves when standing in the same position as the CH_2 of diphenylmethane. This occurs in the case of diphenylamine. The following formulæ show these relationships.



Diphenylmethane.



Diphenylamine.

As diphenylamine has a high fusing point, it could not be examined, but its rotation can be found, with moderate accuracy, by subtracting from methyldiphenylamine the difference due to the displacement of hydrogen in aniline by methyl, thus

Methyldiphenylamine..................	34·878
Less influence of CH_3 disp. H in methylaniline	3·548
Estimated rotation of diphenylamine	31·330

The following shows the relationship of this base to diphenylmethane and also the influence of NH, thus

Molecular rotation of diphenylamine	31·330
,, ,, diphenylmethane ..	23·845
Difference between NH and CH_2.........	7·485
Plus CH_2 in diphenylmethane	1·257
NH	8·742

This is not very much less than twice the influence of NH in aniline (4·792).

Now, the ordinary influence of NH (or NH_2 disp. H) is 0·971, which is less than one-seventh of the above, consequently this group does not act as a screen merely, as CH_2 does to a great extent, but causes a large augmentation of the rotation. If the effect of CH_3 displacing hydrogen in aniline be added to the above estimate of the influence of NH in diphenylamine, that of $N(CH_3)$ in methyldiphenylamine can be found, thus: $8·750 + 3·540 = 12·290$. This is a very remarkable result.

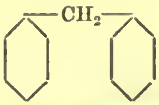
It is impossible to believe that the NH group itself can have risen in rotation from 0·971 to 8·750, or that the $NH(CH_3)$ has become 12·290, but it seems evident that the whole molecules of these two bases must have increased in rotatory power.

It is interesting to notice the effect of introducing CH_2 between the nitrogen and one of the phenyls in diphenylmethane. This occurs in the case of benzylaniline, and shows clearly the screening influence of this group, thus

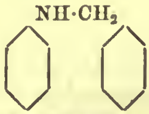
Molecular rotation of diphenylamine	31·330
,, ,, benzylaniline	31·295
	0·045

So that although it contains CH_2 more its rotation is smaller.

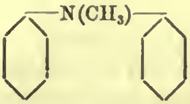
These two bases and methydiphenylamine are related, thus



Diphenylmethane.



Benzylaniline.



Methyldiphenylamine.

Benzylaniline is also interesting in connection with its isomer, methyldiphenylamine; their rotations differ as follows.

Methyldiphenylamine	34·878
Benzylaniline	31·295
	3·583

The extent of the differences between these bases is partially owing to the methyl group in methyldiphenylamine having a very large influence, such as it has in methylaniline, and also to the screening influence of the CH_2 group in benzylaniline keeping the rotation of this base low.

Benzylamine and Dibenzylamine.

The screening effect of the CH_2 group in bases has been referred to above in the case of benzylaniline. The following additional examples give confirmatory evidence of this.

			Diff. for
Molecular rotation of toluene		12·157	1·489, NH_2 disp. H.
,, ,,	benzylamine..	13·646	12·233, $CH_2C_6H_5$ disp. H.
,, ,,	dibenzylamine	25·879	

From the first comparison, it is seen how greatly the intervention of CH_2 in benzylamine, acting as a screen between the C_6H_5 and NH_2, affects the rotation, for, in the case of aniline, the influence of the NH_2 group displacing H amounts to 4·792, and a very similar result is obtained on comparing the toluidines with toluene. This difference of 1·489, however, is higher than that found in the fatty series (0·971), so that the screening effect is not perfect; it is, however, very strongly marked. In the case of the comparison of mono- with di-benzylamine, the difference for the influence of the second $CH_2{\cdot}C_6H_5$ displacing hydrogen is only 12·233, whilst that of phenyl in methyldiphenylamine is 15·254, although containing CH_2 less. This second group, however, as it exists in dibenzylamine, has a greater effect than in toluene, in fact, nearly exactly the same as that in dibenzyl, which gives for $CH_2{\cdot}C_6H_5$ displacing hydrogen 12·234 (thus dibenzyl $= \frac{24{\cdot}977}{2} = 12{\cdot}488$, this when displacing hydrogen would be 0·254 less than this amount or 12·234). That this value is higher than that found in toluene (11·648) is no doubt due as mentioned above, to the phenyl groups in dibenzyl not being perfectly screened from their influence on each other by the $CH_2{\cdot}CH_2$ group.

Benzylamine, when compared with its isomer, orthotoluidine, shows in a very striking manner the influence of the CH_2 group separating the nitrogen from the nucleus.

Molecular rotation of orthotoluidine	17·200
,, ,, benzylamine	13·646
Difference..........	3·554

Phenylhydrazine.

The relationship of phenylhydrazine to aniline may be considered here.

This substance, $C_6H_5{\cdot}NH{\cdot}NH_2$, is usually regarded as aniline with one of the hydrogens of the NH_2 group displaced by NH_2, and from what has already been noticed in reference to the NH_2 group itself, the influence of this displacement becomes interesting. The rotations are as follows.

Molecular rotation of phenylhydrazine ...	18·061
,, ,, aniline	16·076
Diff. for NH_2 disp. H..............	1·985

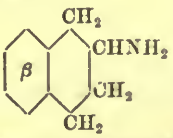
This difference for the influence of the NH_2 group, although about twice as large as it is in the fatty series, is only about two-fifths of what it is in aniline, from which it is evident that the effect of this group $NH{\cdot}NH_2$, when united to phenyl, is far less than twice that of NH_2 when acting alone. This no doubt arises chiefly from one only of the nitrogen groups, being connected with the nucleus, and that this is so, is borne out by comparing it with one of its isomers, thus

Molecular rotation of orthophenylenediamine..	19·391
,, ,, phenylhydrazine	18·061
Difference...............	1·330

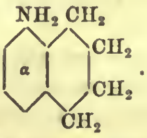
It was on account of this character of the rotation of phenylhydrazine that it was assumed that the largeness of the rotation of phenylazoimide was due chiefly to the influence of the one atom of nitrogen in direct union with the phenyl group (see p. 1098), the other two having a smaller effect.

ar-*Tetrahydro-α-naphthylamine and* ac-*Tetrahydro-β-naphthylamine.*

The influence which the NH_2 group has on the rotation of compounds according to the kind of carbon group it is associated with, is shown on reference to these compounds. Their structures are represented thus



ac-Tetrahydro-β-naphthylamine.



ar-Tetrahydro-α-naphthylamine.

The α-compound may be regarded as a tetramethyleneaniline, the NH_2 group being connected with the unsaturated ring; and the β-compound as a phenylene secondary benzylamine, the NH_2 group being associated with the saturated ring.

Before considering these two compounds, it will be worth while first to see if their rotations are at all what might be expected from their constitution; this, however, can only be done roughly, as the data to work from are insufficient for a very close estimate. The influence of position also affects the rotations.

To split up each of these substances into two compounds the rotations of which are known, it would be necessary to add 4 atoms of hydrogen, thus

$$\underset{\textit{ar}\text{-}\alpha\text{-compound.}}{C_{10}H_{13}N} + H_4 = \underset{\text{Aniline.}}{C_6H_7N} + \underset{\text{Butane.}}{C_4H_{10}}$$

$$\underset{\textit{ac}\text{-}\beta\text{-compound.}}{C_{10}H_{13}N} + H_4 = \underset{\textit{Sec}\text{-butylamine.}}{C_4H_{11}N} + \underset{\text{Benzene.}}{C_6H_6}$$

If this principle be acted on in reference to the rotation, the following results are obtained.

Molecular rotation of *ar*-tetrahydro-α-naphthylamine ..	20·058
Plus H_4	1·016
	21·074
Less aniline	16·076
C_4H_{10}	4·998
Rotation of butane	4·600
Difference between calculated and found rotation......	0·398
Molecular rotation of *ar*-tetrahydro-β-naphthylamine ..	16·147
Plus H_4	1·016
	17·163
Iso- or *sec*-butylamine	5·692
	11·471
Benzene	11·284
Difference between calculated and found rotation......	0·187

From these it is seen that the results are slightly higher than the calculated, but, considering the method used, they are sufficiently near to show that the rotations are consistent with the constitution.

On comparing the rotations of the two bases, the great difference between the influence the NH_2 exerts in them will be seen.

ar-Tetrahydro-α-naphthylamine	20·058
ac-Tetrahydro-β-naphthylamine	16·147
	3·911

This, as might be expected, closely agrees with the difference between the influence of NH_2 in fatty and in aromatic compounds.

Difference in the case of aniline.....	4·792
,, ,, ,, fatty amine	0·971
	3·821

It will be interesting here to compare all the amido-bases which have been examined (containing one nucleus, and with which the nitrogen is in direct union) with the corresponding hydrocarbons or other compounds from which they are derived.

	Mol. rot.	Influence of NH_2 disp. H.
Aniline	16·076	4·792
Benzene	11·284	
Orthotoluidine	17·200	5·043
Toluene	12·157	
Paratoluidine	16·347	4·190
Toluene	12·157	
Metatoluidine..........	16·210	4·053
Toluene	12·157	
Orthoanisidine	18·722	4·764
Anisol................	13·958	
Paraanisidine..........	18·306	4·348
Anisol................	13·958	
Metachloraniline	16·969	4·459
Chlorobenzene	12·510	
Parachloraniline	17·066	4·556
Chlorobenzene	12·510	

These differences are all very large, but they are not regular; this is chiefly owing to the position of the NH_2 in the nucleus not being always the same, as will be seen if aniline and the ortho-compounds, and the meta- and para-compounds, are placed by themselves.

	Diff. for NH_2 disp. H.	
Aniline	4·792	4·866
Orthotoluidine..........	5·043	
Orthoanisidine..........	4·764	
Paratoluidine	4·190	4·364
Paranisidine............	4·348	
Parachloraniline	4·556	
Metachloraniline	4·459	4·256
Metatoluidine	4·053	

Of course perfect uniformity cannot be expected in cases of derivatives of hydrocarbons, oxides, and chloro-compounds, still there is a distinct analogy between them, and it will be found, as in other cases, that, whilst meta- and para-compounds give closely related rotations, those of ortho-compounds are higher.

α- and β-Naphthylamines.—Attention has already been directed to the fact that when benzene is converted into a nitro-compound, it yields a product with a rotation *lower* than that of the parent substance by 1·923, but that when amidated, it is higher by 4·792. In the case of naphthalene, the same changes occur, but are of a much more pronounced character. It has already been seen that the rotation of α-nitronaphthalene is no less than 4·285 *lower* than that of naphthalene; the following shows how much higher the rotation of the α-base is than that of the hydrocarbon.

α-Naphthylamine	37·478
Naphthalene	25·125
Influence of NH_2..	12·353

It is interesting, however, to notice that the numbers, although very different in magnitude, are both in the case of the benzene and naphthalene derivative, relatively not very different, thus

	Nitro-derivative.	Base.	Ratio.
In benzene......	− 1·923	+ 4·792	as − 1 : + 2·491
In naphthalene ..	− 4·285	+ 12·353	as − 1 : + 2·882

The relative rotations of naphthalene and β-naphthylamine are

Molecular rotation of β-naphthylamine ..	35·700
„ „ naphthalene	25·125
	10·575

The variation in the rotations of the α- and β-bases is due to the difference in the positions of the NH_2 group in the hydrocarbon, and is referred to further on; the amounts, however, in both cases are very large considering they are caused by this small group, which, when displacing hydrogen in a paraffin, has an influence on the rotation of only 0·971.

The very large effect produced when the dimethylated amido-group displaces hydrogen in benzene has been already alluded to, but, as other compounds of this class have been examined, it will be useful to compare them altogether, thus

	Mol. rot.	Diff. for $N(CH_3)_2$ disp. H.
Molecular rotation of dimethylaniline	22·888	11·604
,, ,, benzene	11·284	
,, ,, dimethylparatoluidine	22·842	10·685
,, ,, toluene	12·157	
,, ,, dimethylorthotoluidine	18·617	6·460
,, ,, toluene	12·157	
,, ,, dimethyl-β-naphthylamine	47·377	22·252
,, ,, naphthalene	25·125	
,, ,, dimethyl-α-naphthylamine	35·994	10·869
,, ,, naphthalene	25·125	

In the first case, it will be noticed that the difference for the influence of this group is greater than that of benzene itself. In the case of paradimethyltoluidine it is smaller, but approximates to that of toluene; being a *para*-compound, its rotation would be somewhat low. In the case of dimethyl-β-naphthylamine it is nearly twice as large as in any of the other examples, and also approximates to that of the hydrocarbon; but β-compounds, like *para*-compounds, are usually low. In the case of orthodimethyltoluidine and α-dimethylnaphthylamine, a most extraordinary condition of things exists, as these should be higher, and not lower, than the corresponding para- and β-compounds; this matter is further considered on p. 1137. Before leaving the naphthylamines, it will be as well to show the remarkable influence of methylation on these bases themselves.

Dimethyl-β-naphthylamine	47·377
β-naphthylamine	35·700
Effect of $(CH_3)_2$ disp. H_2 in NH_2	+ 11·677

Dimethyl-α-naphthylamine	35·994
α-naphthylamine	37·478
Effect of $(CH_3)_2$ disp. H_2 in NH_2	— 1·484

so that, on comparing the β-compound with naphthalene it is found that the influence of the NH_2 group raises the rotation 10·575, and the methylation further increases it by 11·677.

In the case of the α-compound, however, the influence of the NH_2 group raises the rotation of the hydrocarbon no less than 12·353, but methylation actually *pulls it down* by 1·484; these results also are considered further on (p. 1139).

From the remarkable influence of NH_2 in the naphthylamines and of $N(CH_3)_2$ in β-dimethylnaphthylamine, which are rather more than twice as great as they are in the case of aniline, it seems clear that *both* neuclei of these compounds are equally influenced, although the displacement takes place in one only.

Diamines.

Three of these have been examined, namely, the ortho-, meta-, and dimethylparaphenylenediamines. Although they will be considered further on in reference to the subject of position, they may be here compared with the corresponding hydrocarbon, and the influence of the NH_2 and $N(CH_3)_2$ groups observed, thus

	Mol. rot.	Diff. for $(NH_2)_2$.
Orthophenylenediamine .	19·391	8·107
Benzene	11·284	
Metaphenylenediamine..	18·843	7·559
Benzene	11·284	

As in the other cases, the ortho-compound gives the largest result, but even this is not twice that found in the monamines, otherwise it would be nearly 10; although this is an extremely large difference, it shows that the introduction of the second NH_2 group has not nearly such a great influence as the first. This is best seen by comparing the ortho-compound with aniline.

Molecular rotation of orthophenylenediamine	19·391
,, ,, aniline....................	16·076
Influence of second NH_2	3·315

Similarly it has been noticed that the second NO_2 group when entering benzene has not the same effect as the first.

On account of the high melting point of paraphenylenediamine, its rotation could not be determined, but, from analogy, it is nearly certain that it will not differ much from that of the meta-compound. If, therefore, we compare this with dimethylparaphenylenediamine, the effect of methylation will be fairly well seen, thus

Molecular rotation of dimethylparaphenylenediamine ..	26·239
,, ,, metaphenylenediamine	18·843
Effect of $(CH_3)_2$	7·396

This is even a little more than is caused by the di-methylation of aniline, which gives 6·812; but, of course, the comparison is not strictly accurate, and they may be somewhat closer; at any rate, they are not very different. That the para- and meta-phenylenediamines have closely related rotations is also seen from the rotations of their hydrochlorides (p. 1112).

Hydrochlorides of Monamines.

In a paper on nitrogen compounds, it has been shown that the influence of nitrogen on fatty compounds varies with its degree of saturation, thus, in nitrates, its rotation is smaller than in nitrites (Trans., 1889, **55**, 738). It appeared probable that this kind of difference might exist in the aromatic compounds in a much more pronounced manner, and that probably the high rotation of the aromatic amines might be due partially to the nitrogen being in a tervalent condition. If this should be so, it is clear that the rotation of these compounds should be lower in their salts, such as the hydrochlorides, where the nitrogen is quinquivalent.

The difficulty was, however, to examine hydrochlorides in the anhydrous condition because aqueous solutions would not be likely to give trustworthy results. It was found, however, that the anhydrous hydrochloride of dimethylaniline, although it is a crystalline compound, may be kept in a state of surfusion for some time, and could therefore have its rotation determined. It was also measured in solution, because it was thought probable that the influence of water on its rotation would most likely be similar to that on aniline and other hydrochlorides, and therefore it would give data by which the rotations of these substances, determined in solution, could be approximately translated into those of the dry salts. The following results were obtained.

	Mol. rot.	Diff. due to water present.
Surfused dimethylaniline hydrochloride	18·326	0·720
58·085 per cent. solution in water	17·606	0·255
29·040 ,, ,,	17·351	
Total..........		0·975

In passing, it is interesting to observe that this salt, unlike chloride of lithium and other alkali chlorides, the hydrochlorides of fatty monamines, and hydrochloric acid itself, diminishes in rotation, whilst they increase.

The following is a comparison between the rotation of dimethylaniline hydrochloride, as estimated from that of the base and of hydrochloric acid, and that actually found.

Molecular rotation of dimethylaniline	22·888
,, ,, HCl dry	2·245
	25·133
,, ,, dimethylaniline hydrochloride found ..	18·326
Reduction....................	6·807

It is thus seen that an enormous reduction in the rotation occurs on fully saturating the nitrogen by means of hydrochloric acid.

A solution of aniline hydrochloride containing 43·53 per cent. of the salt was also examined, as this dilution stands about midway between those of dimethylaniline hydrochloride given above, the probable effect of the water being between 0·720 and 0·975 or 0·847. The following is a comparison of the found and calculated results.

Molecular rotation calculated for aniline......	16·076	18·321
Plus HCl (dry)	2·245	
Molecular rotation of 42·53 per cent. solution of aniline hydrochloride....................	15·547	16·394
Plus influence of solution	0·847	
Reduction		1·927

Here also there is a large reduction, although not nearly so great as in the case of dimethylaniline hydrochloride; this, however, is only what might be expected, because the NH_2 group does not exert so large an influence when displacing hydrogen in benzene as does the group $N(CH_3)_2$. The ratio of these two influences is as 1 : 2·421, that of the reduction in the hydrochloride as 1 : 3·532, so that, although the reductions are of the same kind, yet they are not in the same proportion.

It is interesting to compare the rotation of the above hydrochlorides.

Molecular rotation of dimethylaniline hydrochloride..	18·326
„ „ aniline „ ..	16·394
Difference for $CH_2 \times 2$ disp. H_2	1·932

This is nearly the usual amount (2·046) found for this displacement in the fatty series; but as the difference between the bases dimethylaniline and aniline for the same variation in composition is 22·888 − 16·076 = 6·812, an amount equivalent to all the large extra influence methylation gave to aniline beyond the ordinary values of methyl, has disappeared on the base being neutralised with hydrochloric acid.

The rotation of aniline calculated from the hydrochloride is only 14·149 (16·394 − 2·245), and on subtracting from this the rotation of benzene, 14·149 − 11·284 = 2·865 is found for the influence of NH_2 displacing H, whereas in the free base it is 4·792.

The hydrochloride of the paradimethyltoluidines were also examined, solutions containing 69·5 per cent. of $C_9H_{13}N,HCl$ being employed. Taking the influence of the water in these as 0·600, the following results are obtained.

Molecular rotation of dimethylparatoluidine	22·842	25·087
Plus HCl (dry)	2·245	
Molecular rotation found for solution	18·465	19·065
Plus influence of OH$_2$	0·600	
		6·022
Molecular rotation of dimethylorthotoluidine	18·617	20·862
Plus HCl (dry)	2·245	
Molecular rotation found for solution	18·705	19·305
Plus influence of H$_2$O	0·600	
		1·557

In this case again the para-compound falls in rotation enormously, although not quite so much as dimethylaniline; this, however, would probably be on account of its being a para-compound.

With respect to the ortho-compound, which is anomalous (referred to in the section on position), it is remarkable that this anomaly disappears in the hydrochloride, the rotation of both salts being related as ordinary ortho- and para-compounds.

Hydrochloride of Diamines.

Three of these have been examined; the solutions could not be made so strong as in the case of the monamines; they were of the following strengths.

			Per cent. of salt.
Solution of	orthophenylenediamine	hydrochloride	18·264
,,	metaphenylenediamine	,,	20·08
,,	paraphenylenediamine	,,	13·397

From the curve formed by the dry dimethylaniline hydrochloride and its solution, this would make the allowance for the influence of water 1·000 for the two first solutions, and 1·100 for the last.

The following are the results obtained.

		Mol. rot. of dry salt.
Molecular rotation of orthophenylenediamine hydrochloride in solution	21·329	22·329
Plus influence of water	1·000	
Molecular rotation of metaphenylenediamine hydrochloride in solution	20·345	21·345
Plus influence of water	1·000	
Molecular rotation of paraphenylenediamine hydrochloride in solution	20·213	21·313
Plus influence of water	1·100	

Compared with the value of the bases, + 2 mols. of hydrochloric acid, they give

		Diff. from calc.
Ortho- base, 19·391 + 2HCl 4·590 =	24·981	2·652
Found	22·329	
Meta- base, 18·834 + 2HCl 4·590 =	23·433	2·088
Found	21·345	
Para- base, 18·843 + 2HCl 4·590 =	23·433	2·120
Found	21·313	

These differences are, of course, in reference to the union of 2 mols. of hydrogen chloride; if divided by two, to make them comparable with aniline hydrochloride, they show, in the case of the ortho-compound (which is the most suitable to use, for reasons given in another part of this paper), that the effect is apparently smaller, namely, 1·326, whereas in aniline it is 1·927; this, however, is not a fair comparison, because as the first and second introduction of the NH_2 group into benzene affect it differently, it is most likely that the hydrochloric acid may act in a similar manner, the first molecule added influencing the rotation more than the second.

As in the case of the monamines, the rotations of these bases are much lower in their hydrochlorides than when they are in the free state. This will be seen from the following table, as well as the influence of the NH_2 group.

Molecular rotation of orthophenylenediamine	19·391
Less reduction when in hydrochloride	2·652
Molecular rotation of orthophenylenediamine in combination	16·739
,, ,, benzene	11·284
(NH_2) disp. H	2)5·455
NH disp. H	2·727

This is much the same as that found in aniline when in combination, namely, 2·865, and perhaps the analogy is closer than this because the above assumes that these groups have both exerted the same influence on the rotation; this, however, as already mentioned, is not the case, and it is not improbable that one might be about 2·865, the same as in aniline, and the second, 2·590, which would agree with the numbers 5·455 the same of both.

The principal change which takes place when a base is converted into its hydrochloride is the saturation of the nitrogen, and it has already been shown that nitrogen in a quinquivalent combination acts differently from that in a tervalent in the case of the fatty series, although the effect is not very large (Trans., 1889, **55**, 737); that it should be much larger in the aromatic series is only in accord with many of the results already discussed. Moreover, that the saturation of the nitrogen should reduce the rotation is in harmony with all the results hitherto obtained with saturated and unsaturated compounds.

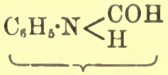
Amides and Anilides.

The following is a comparison of the products of this kind which have been examined.

	Mol. rot.	For diff. of constitution.
Formanilide	15·211	1·691
Benzamide	13·520	
Acetanilide	16·003	0·795
Phenylacetamide ($C_6H_5{\cdot}CH_2{\cdot}CONH_2$)	15·208	

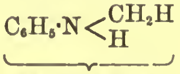
The last difference is much smaller than the first, and it is not improbable that there should be this difference; as, however, much difficulty was experienced in determining the rotation of the last pair of compounds, the results are not given with much confidence, except that there is no doubt as to the anilide having by far the larger rotation, and in this both sets of examples agree.

The rotation of formanilide, although it contains CO more in its composition, has a lower rotation than that of orthotoluidine by 1·989, being another example of the influence this group has in reducing the rotation of a compound; a still greater difference will be found if it is compared with methylaniline, which it represents as having the CH_2 of the methyl group displaced by CO, thus



$$\underbrace{C_6H_5{\cdot}N{<}{}^{COH}_{H}}$$

Formanilide.



$$\underbrace{C_6H_5{\cdot}N{<}{}^{CH_2H}_{H}}$$

Methylaniline.

In this case, the rotations differ greatly.

Methylaniline	19·624
Acetanilide	16·003
Reduction for CO disp. CH_2 in CH_3.	3·621

The same applies to acetanilide (assuming its rotation to be not far from the truth), which only differs from ethylaniline in having CH_2 displaced by CO, but on comparing them in this way there is a difference of no less than about 4·565.

In the first case, the CO has fully destroyed the large influence methyl has in methylaniline (3·548), and in the second, it has destroyed that of the ethyl in ethylaniline (4·491).

Benzamide may be compared with benzylamine, in which CH_2 has been displaced by CO, thus

$C_6H_5{\cdot}CH_2{\cdot}NH_2$. Benzylamine.

$C_6H_5{\cdot}CO{\cdot}NH_2$. Benzamide.

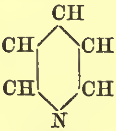
Here the difference is small.

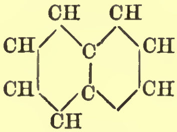
Molecular rotation of benzylamine ..	13·646
,, ,, benzamide	13·520
Reduction for CO disp. CH_2	0·126

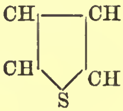
The difference in the valne found for CO displacing CH_2, on comparing propylamine and propionamide, is 0·194, so that the above difference is a little less than this, and the phenyl united with the CH_2 has a slight augmenting influence in benzylamine, which has also been removed; it seems, therefore, that although the NH_2 group is separated from the C_6H_5 by means of CO, yet a small amount of influence passes through it, and slightly raises its rotation.

Pyridine, Quinoline, and Thiophen.

The constitution of these substances is usually represented thus


Pyridine.


Quinoline.


Thiophen.

Thus showing them to have a general analogy to aromatic compounds but with nitrogen and sulphur substituted for a carbon atom in the nucleus.

The low refractive power of these substances has, however, always been a difficulty in connection with this view, and the determinations of the magnetic rotations increase this, as the following comparison of their rotations with those of the hydrocarbons they are supposed to represent, will show.

	Mol. rot.		Mol. rot.
Pyridine	8·748	Benzene	11·284
Quinoline........	20·875	Naphthalene ..	25·125
Thiophen	9·575		

Thus it is seen that in the first two examples the rotations are much lower than those of the hydrocarbons, although they contain nitrogen, which in bases so greatly augments their rotation; when it is remembered also that sulphur has a very large influence on rotations, the low numbers obtained for thiophen are likewise very striking.

These rotations are, therefore, at variance with the above views regarding the character of these substances.

Pyridine.—Some time ago, the rotation of piperidine, as well as that of pyridine, was examined (Trans., 1889, **55**, 735), and it was noticed that the difference between the numbers obtained from these compounds for the difference of saturation by H_6, amounted to 2·951, or about three times the difference existing between saturated and unsaturated fatty compounds differing in composition by H_2.

Since then the series of hydrocarbons of different degrees of saturation between hexane and dipropargyl have been examined (Trans., 1895, **67**, 262—263), and here the difference for H_6 which exists between the rotation of hexane and dipropargyl is found to be 2·962, or almost exactly the same as that between piperidine and pyridine; or if that between hexane and C_6H_8 is taken, it is 2·754, or only a trifle less. The inference is, therefore, that the rotation of pyridine is of the same kind as that of an *open* chain compound, although it is represented as a ring.

It is as well to point out here that the analogy between these bases and the hydrocarbons is not quite perfect, because in the one case the difference for unsaturation is connected with $C_5 + N$, whereas in the other it refers solely to C_6. Still, at the same time, the linking in both cases is of the same kind, namely, –CH⁚N– and –CH⁚CH–.

Now in what respect do open and closed chain compounds differ in rotation? One of the most striking differences is in the relative character of their saturated and unsaturated compounds. Above, it is seen that in the open chain compounds there is an increase of 2·951 for a loss of H_6, but for the same difference, in the case of hexahydrobenzene and benzene, it is about 4·851, or nearly twice as much.

Now the circumstance which brings about all this difference results from the two ends of an unsaturated open chain being united with each other. For instance, if the ends of a chain compound of the structure $CH_2⁚CH·CH⁚CH·CH⁚CH_2$, were to unite with loss of H_2, benzene would be produced, thus forming a symmetrical cycloid.

An unsaturated and a closed chain are in some respects comparable with a chain and a circle of bar electromagnets. In the latter, as is well known, the force necessary to rupture the open chain is much smaller than that required to break the closed chain. Now if from a closed chain of magnets one be removed, and for it be substituted a bar of some non-magnetic material, it is evident that the magnetic effect will simply be that of an open chain, although it appears to be a closed one, because one of its elements is of a different nature from the others.

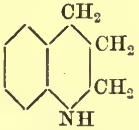
This seems to be the condition of things in pyridine. One carbon group of the benzene ring has been displaced by nitrogen, which, although holding the ring together, is a foreign element between the carbon atoms it unites, and therefore the product has not the high rotation of a closed carbon chain. This also explains why the difference between the rotations of piperidine and pyridine is similar to that existing between hexane and dipropargyl.

Quinoline.—With regard to this base, there can be but little doubt that it is not a true representative of naphthalene, which consists of two closed carbon groups, for its molecular rotation is 4·250 lower than that of the latter, as may be seen from the foregoing table.

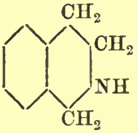
The difference between quinoline and its tetrahydro-compound is relatively smaller than that between pyridine and piperidine, thus

	Mol. rot.
Quinoline....................	20·875
Tetrahydroquinoline	19·619
Diff. for unsaturation by H_4	1·256

The difference for H_6 in the previous instance was 2·951, or, taking two-thirds of this for H_4, 1·975; the difference also between dipropargyl and diallyl is 2·015 for H_4. Tetrahydronaphthalene has not yet been examined, so that the difference between this and naphthalene is not known, but the smallness of this difference is probably due to the nitrogen of quinoline being in direct union with the unsaturated nucleus as well as with the saturated, as it is found that the difference between *ar*-tetrahydro-α-naphthylamine and α-naphthylamine is smaller than is found in the case of the *ac*-tetrahydro-β-compound and β-naphthylamine, the amounts being 17·420 and 19·535 respectively (numbers out of all proportion to those of the quinoline compounds). Isoquinoline and its tetrahydro-derivative would, therefore, probably give a larger difference, as the nitrogens in these compounds are quite separated from the unsaturated nucleus, thus



Tetrahydroquinoline.



Tetrahydroisoquinoline.

Thiophen.—As previously mentioned, this compound has such a low rotation that, like pyridine and quinoline, it cannot be considered as a true aromatic closed chain compound with sulphur representing two carbon groups. If, however, it be regarded from the same point of view as pyridine, the numbers it gives are intelligible.

The effect of the hydrocarbon portion of pyridine may be estimated thus

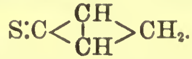
	Mol. rot.
Pyridine..............	8·748
N as in amines	0·717
C_5H_5	8·031

This is a low value for this product, but it must be remembered that the rotation of piperidine is also low (Trans., 1889, **55**, 733).

If a fifth of this be subtracted, the value of C_4H_4 will be obtained, namely, 6·441, which represents the hydrocarbon constituent of thiophen, and if this be taken from the rotation of this substance, an estimate of the influence of sulphur will be found, thus

	Mol. rot.
Thiophen	9·575
Less C_4H_4	6·441
S =	3·134

The influence of sulphur varies very much in different compounds. In the free state, the octahedral variety has a rotation of 4·856, whilst in combination with carbon in carbon bisulphide, it is about 5·08, but in ethylic sulphide only 3·283, which is close to the above estimate, and therefore renders it quite a probable amount.

Thomsen (*Thermochemische Untersuchungen*, **4**, 342) seems to have found a difficulty in regarding this substance as comparable with benzene, and proposes for it the formula,  $S{:}C<\begin{smallmatrix}CH\\ |\\ CH\end{smallmatrix}>CH_2$.

Whilst the intervention of the nitrogen and sulphur in these compounds between the carbon groups prevents them from having the physical properties of closed carbon chain compounds, this kind of combination evidently gives them great stability.

Owing to the want of data, the above calculations in reference to these bases and thiophen can only be regarded as somewhat rough approximations, but still they serve their purpose fairly well, because they give an intelligible meaning to the magnetic rotation and refractive power of these compounds.

It is interesting to notice that both nitrogen and sulphur, when interfering with the symmetry of a cyclic compound by separating the carbon groups, act as a screen, and keep the rotation low, whereas when outside the closed chain, and attached directly to one of its carbons, they cause the rotations to be large, as seen in phenylazoimide, phenylic sulphide, &c.

Haloïd Compounds containing the Benzene Nucleus.

Benzene Derivatives.—Four of these have been examined, the following being their names and rotation.

	Mol. rot.	Diff.
Fluorobenzene............	9·970	2·540
Chlorobenzene............	12·510	1·996
Bromobenzene............	14·506	4·602
Iodobenzene	19·108	

Fluorobenzene.—This is the only fluorine compound which has hitherto been examined. The result is interesting and remarkable, because the rotation is so much lower than that of benzene itself (11·284), and even than that of its open chain isomer, dipropargyl (10·435); the introduction of this element, therefore, in place of hydrogen, has caused a reduction of 1·324, or an amount rather more than five times the value of the hydrogen displaced. From this it is evident that the rotation of fluorine in combination with the nucleus, like NO_2, has a negative influence. The molecular rotation of this compound is only a little higher than that of nitrobenzene (9·361).

Chlorobenzene.—The following is a comparison of the calculated and observed rotations of this compound.

Molecular rotation of benzene	11·284
Chlorine, disp. H, as in propylic chloride..	1·479
	12·763
Molecular rotation found	12·510
Difference	− 0·253

Here the rotation is also somewhat lower than the calculated.

Bromobenzene.—The following is the calculated value of this compound.

Benzene	11·284
Bromine, disp. H, as in propylic bromide.	3·308
	14·592
Molecular rotation found	14·506
Difference	− 0·086

This result shows a very small difference between the calculated results and those found.

Iodobenzene.—The calculated value of this is as follows.

Benzene	11·284
Iodine, disp. H, as in propylic iodide.....	7·503
	18·787
Found	19·108
Difference	+ 0·321

In this case the result found is higher than the calculated.

These four haloïd compounds of benzene form a curious and interesting series, because when the haloïd has a very low rotation, as no doubt it has in the case of fluorine, the derivative has actually a much lower rotation than the hydrocarbon itself; on the other hand, where it is not so low, as in the case of chlorine, the rotation, although less than the calculated, begins to approach it; again, where it is about the same, as with bromine, the rotation of the product is practically the same as the calculated, but where it is above, as in the case of iodine, the rotation of the iodo-derivative is above that calculated, making it appear as if these peculiarities were all due to the relationship of the rotation of the halogen to that of the hydrocarbon. These were some of the results which made me examine mixtures of substances having the same and different specific rotations, but whether the remarkable differences in the rotations of these haloïd derivatives is at all due to this appears to be doubtful.

Paradichlorobenzene.

The rotation of this compound appears at first sight to be low, as will be seen from the following comparisons.

	Mol. rot.	Diff. for Cl disp. H.
Paradichlorobenzene	13·655	1·145
Chlorobenzene	12·510	1·226
Benzene	11·284	

It has already been noticed that the rotation of chlorobenzene is lower than might be expected, by 0·253, and from the above it would seem that this second displacement was of the same character, as the value of chlorine displacing hydrogen is 1·479; it must be remembered, however, that the second displacement is in the para-position, and, judging from analogy, if it had been in the ortho-position it would have been about 0·473 higher, which would raise the difference to 1·516. Now ortho-compounds have rotations which are nearly the same as those of ordinary mono-benzene derivatives, in which relative position does not occur, so that the comparison in the above table gives a false idea of the influence of the second displacement by chlorine, because the rotations of the para-compounds are relatively lower than those of monosubstituted benzene compounds. Taking the effect of position into account, the rotation of paradichlorobenzene indicates that the second displacement of hydrogen by chlorine is of about the ordinary kind (as in the fatty series), and has not been attended with any contraction in the rotation like that of the first displacement.

Benzylic Chloride, $C_6H_5\cdot CH_2Cl$.

The rotation of benzyl compounds has been found in the cases of benzylic alcohol and benzylamine to be lower than their isomers the cresols and toluidines. Benzylic chloride, however, gives a higher rotation than the chlorotoluenes; thus, comparing it with the chlorotoluene having the highest rotation, namely, the ortho-compound, the following difference is obtained.

Molecular rotation of benzylic chloride ..	14·014
,, ,, orthochlorotoluene	13·719
Difference	+ 0·295

This, however, is not remarkable, if it be borne in mind that in benzylic chloride the chlorine is in union with the CH_2 group only, whereas in orthochlorotoluene it is in the nucleus, and this, as shown in the case of chlorobenzene, reduces its influence by 0·253; as no reduction would take place on the formation of benzylic chloride, its rotation would be expected to be that much higher than the rotation of orthochlorotoluene. This is only a very little less than that found.

It is of interest to notice that it is rather lower than half that of dibenzyl, *plus* chlorine.

Half molecular rotation of dibenzyl......	12·488
,, ,, chlorine	1·733
Benzylic chloride (calc.)	14·221
Found	14·014

Ortho- and Para-chlorotoluenes and bromotoluenes.

Both the ortho- and para-chlorotoluenes and bromotoluenes have been examined, but their rotations cannot be discussed here; they will be found in the section on the influence of position (p. 1131).

Benzoic Chloride, $C_6H_5{\cdot}COCl$.

From what has been previously noticed, this substance may be regarded as acetic chloride in which methyl is displaced by phenyl, rather than as formic chloride with hydrogen displaced by this group. The influence of chlorine in acetic chloride is estimated as 1·669, whilst that of carbonyl is believed to be about 0·850 (Trans., 1894, **65**, 105). The effect of CO·Cl will then be 2·519, and if this be subtracted from the rotation of benzylic chloride, it should give that of C_6H_5 thus

Molecular rotation of benzoic chloride....	12·383
Less CO·Cl	2·519
C_6H_5	9·864

This is a very low number for phenyl. In benzophenone, the effect of carbonyl is to reduce the phenyl to 10·100, and in benzaldehyde and ethyl phenyl ketone it is only a little higher, but in this case the influence of CO·Cl is greater, supposing that this group in benzoic chloride has the influence here assigned to it. There can be no doubt the rotation is a very low one, because if compared with benzaldehyde it shows too small a difference for chlorine displacing hydrogen, thus

Molecular rotation of benzoic chloride....	12·383
" " benzaldehyde......	11·844
Effect of Cl disp. H	0·539

This number is about 0·934 too low, so that the group CO·Cl evidently has a very considerable reducing influence on the rotation of this compound.

It may also be compared with acetic chloride, thus

Benzoic chloride	12·383
Acetic chloride	3·800
C_6H_5 disp. CH_3	8·583
CH_3 (about)..............	1·277
C_6H_5	9·860

This agrees closely with the number previously obtained for this group.

Phenylacetic Chloride, $C_6H_5 \cdot CH_2 \cdot COCl$.

This differs from the previous compound in having CH_2 to screen off the influence of the CO·Cl from the phenyl, and the effect is very striking if compared with benzoic chloride; it gives a large difference for variation in composition.

Phenylacetic chloride..................	14·091
Benzoic chloride	12·383
Diff. for CH_2	1·708

This is considerably above the usual effect of CH_2, and shows how this group has prevented the reducing influence of this CO·Cl from affecting the nucleus.

If this substance be compared with propionic chloride, and allowance made for the methyl group, it gives

Phenylacetic chloride..................	14·091
Propionic chloride	4·753
C_6H_5 disp. CH_3	9·338
CH_3	1·277
C_6H_5	10·615

This result is not very different from that found in the case of the ethereal salts of the aromatic acids, which gives 10·457 for C_6H_5, disp. H, or 10·711 for the group itself (see p. 1078).

Phenylsulphonic Chloride, $C_6H_5{\cdot}SO_2Cl$.

This is the only substance of this class which has been examined; the nearest compound with which to compare it is benzoic chloride, the difference between the two being that the latter contains CO in place of SO_2.

Molecular rotation of benzenesulphonic chloride	14·167
,, ,, benzoic chloride	12·385
Diff. = SO_2 disp. CO..........	1·782
Plus CO	0·850
Rotation of SO_2	2·632

The value of SO_2 deduced from SO_2Cl_2 is about 2·454, which is not far from the above, so that the rotation of the substance is apparently normal.

Sulphur Compounds.

Carbon Bisulphide, CS_2.

As this substance is referred to in connection with some of the aromatic compounds, its rotation may be considered here; its molecular rotation at 15° is 10·751; if from this the value of carbon deduced from the paraffin be taken, namely, 0·515, it leaves for the value of sulphur 10·236/2 = 5·118.

The effect of the group –CS– on the rotations of the various compounds in which it exists, will then be probably about the same as that of CS_2 less S, 10·751 − 5·118 = 5·633, or displacing H_2, 5·633 − 0·508 = 5·125.

Phenylic and Benzylic Sulphides, $C_6H_5{\cdot}S{\cdot}C_6H_5$, *and* $C_6H_5{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}C_6H_5$.

The rotation of sulphur itself and some of the different influences it exerts on the rotation of compounds has already been referred to when considering the rotation of thiophen, but when in direct union with the nucleus as in phenylic sulphide, its effect would be expected to be considerably enhanced; this is evidently the case from the high rotation of this compound, which is even higher than that of benzylic sulphide, although the latter contains CH_2 more in its composition, thus—

Molecular rotation of phenylic sulphide ..	29·668
,, ,, benzylic sulphide ..	29·216
Difference................	0·452

Comparing the rotation of phenylic sulphide with that estimated for two phenyl groups, as calculated from benzene, the effect of the combination of these with sulphur is seen to be very great.

Molecular rotation of phenylic sulphide	29·668
,, ,, C_6H_5 × 2 = 10·776 × 2....	21·552
Influence of sulphur	8·116

Making a similar comparison in the case of benzylic sulphide, calculating the effect of $CH_2{\cdot}C_6H_5$ from toluene, the following result is obtained.

Molecular rotation of benzylic sulphide	29·216
,, ,, $CH_2{\cdot}C_6H_5$ × 2 = 11·903 × 2	23·806
Influence of sulphur	5·410

In the first case, there can be no doubt that 8·176 does not represent the rotation of sulphur in this compound, but shows that this element when in direct union with phenyl (as in the case of NH_2) causes the rotation of the product as a whole to be greater than that of the sum of any of the ordinary values of phenyl and sulphur.

In the case of benzylic sulphide, the screening influence of the CH_2 groups which come between the sulphur and phenyl is very striking; it is possible, however, that this is not perfect, and that they still influence each other to a small extent through these groups, for it should be noted that 5·410 is apparently a higher rotation than sulphur is likely to possess.

Thiocarbanil, $C_6H_5{\cdot}N{\cdot}CS$.

The data for studying the rotation of this compound are not very satisfactory; it may be represented as aniline with H_2 displaced by CS, and, therefore, by subtracting from its rotation that of aniline, a residue will be obtained representing the influence of CS displacing H_2, which may be compared with that estimated from carbon bisulphide, namely, 5·125, thus—

Molecular rotation of thiocarbanil	21·526
,, ,, aniline............	16·075
CS disp. H_2	5·451

This is rather higher than the above, but the association of this group with phenyl and nitrogen might enhance its influence. So far as can be seen, therefore, from the above, the rotation of thiocarbanil is likely to be consistent with its structure.

SECTION III.—ON SOME OF THE RELATIONSHIPS OF THE ROTATIONS OF AROMATIC COMPOUNDS.

The study of this subject, which is important for several reasons, is not very easy, because it is necessary to discriminate between the compounds which may be considered normal and those which appear to be abnormal. At first this presented some difficulty, but the following plan seems satisfactory as far as it goes.

In the fatty series, it has been found that there are certain variations between the rotations of different classes of compounds, because each has a special series constant. Thus, taking the propane derivatives as an example, we get—

	Mol. rot.	Diff.
Molecular rotation of propane (calc.)....	3·577	
,, ,, propylic alcohol ..	3·768	+ 0·191
,, ,, propaldehyde	3·332	− 0·436
,, ,, ethylic propionate	5·452	+ 2·120

The same differences are found on comparing the higher homologues of these substances. Now, as analogous aromatic compounds represent fatty substance with one atom of hydrogen displaced by phenyl, it was to be expected that similar relationships might be found to exist in them, with small variations due to phenyl not having exactly the same value in these different classes of compounds, owing to the influence of the groups it is associated with; from the following comparison, this is evidently the case, thus

	Mol. rot.	Diff.
I. Toluene	12·157	
Benzylic alcohol	12·400	+ 0·243
Benzaldehyde	11·864	− 0·536
Ethylic benzoate	13·854	+ 1·990
II. Paramethylisopropylbenzene	15·255	
Cuminic alcohol	15·879	+ 0·624
Cuminaldehyde	15·245	− 0·634
Ethylic cuminate	17·093	+ 1·848

In the next examples, the comparisons are made between unsaturated compounds. Amongst those selected, cinnamaldehyde and ethylic cinnamate are *trans* or *fumaroid* compounds; and it will, therefore, be necessary to subtract 0·468 from their rotations (see p. 1145) to make them comparable with the other ordinary members of the series.

	Mol. rot.	Diff.
III. Allylbenzene	17·599	+ 0·341
Cinnamic alcohol	17·940	− 0·523
Cinnamaldehyde (17·885 − 0·468)	17·417	+ 2·121
Ethylic cinnamate (20·006 − 0·468)	19·538	

All the substances in the previous examples contain phenyl or methylated phenyl, but in the following table hydroxy-derivatives are compared.

	Mol. rot.	Diff.
IV. Orthocresol	13·382	+0·525
Salicylic alcohol (estimated from the methyl derivative)	13·907	−0·621
Salicylaldehyde	13·286	+2·080
Ethylic salicylate	15·366	

In the first three examples, the alcohol is seen to be a *plus* quantity in each case as compared with the hydrocarbon, the aldehyde a *minus* quantity as compared with the alcohol, and the ethereal salt a *plus* quantity as compared with the aldehyde; the last must obviously be so, because the substance contains two atoms more carbon than the others, due to the ethyl, but in all instances the plus and minus differences accord quite as well as could be expected, both in the series which contain C_6H_5 as also in those in which displacements exist, such as the para- and otho-compounds. No sufficiently complete series of meta-compounds has been examined, but there is no reason to think they would be exceptions. The above tables therefore show that a close analogy exists between the aromatic and fatty series; this is very interesting, and indicates, moreover, that the determinations of the rotations are evidently near to the truth.

From the above relationships, the rotations of the aromatic compounds given may be considered normal, so that in any other similar sets of examples, which do not show analogous differences, it may be considered that they are abnormal owing to some other influence coming into play; for instance, it has already been noticed that in the methyl displacements in the amines peculiar irregularities in the rotations exist. It will therefore be important to consider the rotation of hydroxy-derivatives in which the hydrogen of the hydroxyl is displaced by methyl, as shown in Table V.

The fluctuations are larger than can be accounted for by experimental error, and are no doubt real, nevertheless, although the ortho-compounds give a rather lower difference than the para- and meta-compounds, yet the differences may be considered to agree fairly well. This, however, is not found to be the case with the examples given in Table VI.

	Mol. rot.	Diff.
V. Phenyl methyl oxide	13·958	1·818
Phenol	12·140	
Orthotolyl methyl oxide	15·190	1·808
Orthocresol	13·382	
Paratolyl methyl oxide	14·712	1·843
Paracresol	12·869	
Metatolyl methyl oxide	14·646	1·870
Metacresol	12·776	
Ethylic methylsalicylate	17·156	1·790
,, salicylate	15·366	
Average		1·826

	Mol. rot.	Diff.
VI. Methylsalicylaldehyde	14·187	0·901
Salicylaldehyde	13·286	
Guaiacol	14·689	1·667
Pyrocatechol*	13·022	
Veratrol	16·837	2·148
Guaiacol	14·689	
Creosol	15·405	2·099
Homopyrocatechol	13·306	
Isocreosol	15·021	1·715
Homopyrocatechol	13·306	
Dimethylhomopyrocatechol	17·484	2·079
Creosol	15·405	
Dimethylresorcinol	15·108	2)2·823
Resorcinol*	12·285	1·411
Trimethylpyrogallol	17·201	3)4·172
Pyrogallol*	13·029	1·390

As widely different results are in some cases obtained, these must be due to some cause other than the simple displacement of hydrogen by methyl. In the displacements in the phenols, the amount is about twice as high as in the fatty series, which is remarkable. In methylsalicylaldehyde it is about the same as in the fatty series.

The differences in the following series of methylated derivatives will be seen not to agree with those previously found in the case of the initial compounds, the expected rotations estimated from the differences given in Table VI being introduced to show where the inconsistencies exist.

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* The rotations of pyrocatechol, resorcinol, and pyrogallol are calculated from the aqueous solutions, and therefore may not be quite so accurate as the other numbers (see pp. 1184, 1185).

VII.

	Mol. rot.	Diff.	Mol. rot. expected from analogy.	Diff.
Orthotolyl methyl oxide	15·190	−0·362	15·190	—
Methylsalicylic alcohol (methyl saligenin)	14·828	−0·641	15·715	0·887
Methylsalicylaldehyde	14·187	+2·969	15·094	0·907
Ethylic methylsalicylate	17·156		17·174	+0·017

The want of agreement in the case of methylsalicylaldehyde is evidently due to methylation, because it does not exist in the non-methylated aldehyde (see Table IV), and it has been seen that the influence of the methylic displacement in this compound is only 0·901, whereas in orthotolyl methyl oxide it is 1·808, and in ethylic methylsalicylate 1·790, or practically the same, the average being 1·799. In methylsalicylic alcohol the methylation probably influences its rotation also to about the same extent as in the aldehyde, namely, 0·901, because if the difference between this and 1·799, or 0·898, be added to the rotation it becomes 15·726, or about the expected number; and this is very probable, because the relationship of this alcohol and the aldehyde in the above Table VII is about the same as is found in other similar comparisons, namely, 0·641.

The next series consists of methylated para-compounds, the estimated difference being calculated from the series of compounds for the same position given in Table II.

VIII.

	Mol. rot.	Diff.	Expected Nos.	Diff.
Paratolyl methyl oxide	14·712	+0·695	14·712	—
Anisic alcohol	15·407	+0·465	15·336	0·071
Anisaldehyde..................	15·872	+1·413	14·702	1·170
Ethylic anisate*	17·285		16·550	0·735

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* On account of this peculiar rotation of ethylic anisate, an endeavour was made to measure a non-methylated compound of parahydroxybenzoic acid. The only product which appeared to be available for this purpose was the methylic salt, which is said to melt at 17° and boil at 283° (Ladenburg and Fitz, *Annalen*, 1867, **141**, 250),

In this set of examples, the two first numbers show much the same relationship as those existing between paramethylisopropylbenzene and cuminic alcohol, and may be considered normal in their rotation (see Table II, p. 1125), but the third and fourth have remarkably high rotations, and judging from the influence of methylation on paracresol (1·843), the methylation in the case of anisic aldehyde must have influenced its rotation about 3·013 (1·843 + 1·170), and in ethylic anisate about 2·578 (1·843 + 0·735). The remarkable rotation of these two compounds is at present inexplicable. Their molecular refractions are also very high.

From the comparisons in Table V (p. 1127), it is seen that in many aromatic compounds the displacement of the hydrogen of hydroxyl by methyl raises the rotation by about 1·800, yet, as shown in Table VI (p. 1127), there are some cases in which its influence is less, and in a considerable number of others where it is greater than this, these fluctuations being due in most cases to some cause at present not understood. It is unsafe, therefore, in making generalisations such as those following, to employ the rotations of compounds of this kind.

Influence of the Ortho-, Para-, and Meta-positions, and also of the α- and β-positions in the Naphthalene Series, on the Rotations.

I. *Ortho-, Meta-, and Para-positions.*

From the foregoing section it is evident that in considering this subject of position it will be necessary to exclude many of the methylated hydroxy-derivatives.

The following are some comparisons of the rotations of compounds belonging to different classes which may safely be used in considering this subject. The first consists of the cresols, and in their case the methyl group has already been shown to have much the same influence in all cases.

Phenols.

	Mol. rot.	Diff.
I. Orthocresol	13·382	
		-0·513
Paracresol	12·869	
		-0·093
Metacresol	12·776	

but on preparing this compound, both from the potassium salt and methylic iodide dissolved in methylic alcohol, and also from the acid itself, methylic alcohol, and hydrochloric acid, it was obtained as a beautifully crystalline solid, forming large crystals, with a solidifying point of 122°, and boiling with slight decomposition at 305° under a pressure of 745 mm. This high fusing point made it unsuitable for a determination of the rotation. As its properties were different from those described by Ladenburg and Fitz, it was subjected to analysis, and gave—

	I.	II.	$C_8H_8O_3$.
Carbon	62·90	62·95	63·15
Hydrogen	5·39	5·46	5·26.

Dihydroxyphenols.

II.	Pyrocatechol	13·022	−0·737
	Resorcinol	12·285	

This difference may possibly be less accurate than the others, as the rotations of the substances are calculated from those of their aqueous solutions, still it is of the same order as the usual difference between ortho- and para-compounds.

Oxides.

		Mol. rot.	Diff.
III.	Orthotolyl methyl oxide	15·190	−0·478
	Paratolyl „ „	14·712	−0·066
	Metatolyl „ „	14·646	

In these examples, the *ortho*-compound is shown to have considerably the highest rotation, whilst the *meta-* is nearly the same as the *para-*, but a trifle higher.

Hydrocarbons.

		Mol. rot.	Diff.
IV.	Orthoxylene	13·345	−0·535
	Paraxylene	12·810	+0·049
	Metaxylene	12·859	

This comparison again shows similar differences, except that the meta-compound is slightly higher than the para-, which is unusual.

The following is a more complex example, but the compounds evidently stand to each other as ortho- and meta-derivatives, because pseudocumene being a 1 : 3 : 4- and mesitylene a 1 : 3 : 5-compound, the two first numbers are the same.

	Mol. rot.	Diff.
Pseudocumene	13·998	−0·632
Mesitylene	13·366	

The result is similar to the other examples, although a trifle higher than in the xylenes.

Ethereal Salts.

		Mol. rot.	Diff.
V.	Ethylic methylsalicylate	17·156	−0·477
	„ metamethoxybenzoate	16·679	
	„ orthotoluate	15·065	−0·321
	„ paratoluate	14·744	

The ortho-compound again, in all these cases, has the largest rotation. In the first instance, the difference is about the same as that found between the ortho-, para-, and meta-tolyl methyl oxides and xylenes, whilst in the latter the difference is rather smaller than in the previous examples.

Nitro-compounds.

		Mol. rot.	Diff.
VI.	Orthonitrotoluene	10·806	−0·592
	Paranitrotoluene	10·214	

Again the ortho- gives the largest rotation.

Halogen Compounds.

		Mol. rot.	Diff.
VII.	Orthochlorotoluene............	13·719	−0·473
	Parachlorotoluene.............	13·246	
	Orthobromotoluene	15·674	−0·507
	Parabromotoluene.............	15·167	
	Parachloraniline	17·066	−0·097
	Metachloraniline...............	16·969	

These show similar differences between the ortho- and para-, and again the meta- is slightly lower than the para-compound.

Bases.

		Mol. rot.	Diff.
VIII.	Orthoanisidine................	18·722	−0·416
	Para-anisidine	18·306	
	Orthophenylenediamine........	19·391	−0·548
	Metaphenylenediamine.........	18·843	
	Orthotoluidine................	17·200	−1·012
	Paratoluidine.................	16·188	+0·022
	Metatoluidine	16·210	

In these instances, orthotoluidine stands out in a very prominent manner, just as the influence of the NH_2 group is very large in the base. The reason why anisidine does not do so as strongly is probably due to its containing oxygen.

The metatoluidine is seen to give very slightly higher results than the para-compound.

It is rather remarkable that diamines do not show a larger difference for position, but it has been noticed that although the first introduction of the NH_2-group greatly affects the rotation, yet that of a second does not influence it nearly so much. The same kind of result evidently occurs in reference to position.

Hydrochlorides of the Bases determined in Aqueous Solution.

These give the following results.

	Mol. rot.	Diff.
Hydrochloride of dimethylorthotoluidine ...	18·705	−0·240
" " dimethylparatoluidine....	18·465	
Diff.	0·240	

The difference is of the ordinary kind, but smaller than usual. It is a very remarkable result, because the rotation of the bases themselves are relatively so dissimilar.

	Mol. rot.	Diff.
Hydrochloride of orthophenylenediamine...	21·329	−1·116
„ „ paraphenylenediamine ...	20·213	+0·132
„ „ metaphenylenediamine ...	20·345	

With these hydrochlorides, the difference for the ortho-position is of the same kind, but about twice as large as usual, whilst the meta- and para-compounds, as in other cases, do not vary much, except that the meta- is rather higher than the para-compound. In all these hydrochlorides, and especially in the latter, which are dihydrochlorides, the variations in the amount of the differences may be due to the influence of the water on them not being the same in all cases.

From the large number of differences given, it is seen that ortho-compounds have considerably higher rotations than para- and meta-compounds. Excluding orthotoluidine, which has an exceptionally high rotation, and also those numbers resulting from the examination of substances in aqueous solution, which, although showing the influence of the ortho-position as the others do, may not be quite so trustworthy, the remaining 10 differences are found to vary between 0·622 and 0·417, the average being 0·517; whilst in the case of the meta- and para-positions, the variations are very small, the meta-compound in some cases being the lower, but in others the para-.

In one set of comparisons, it is difficult to know how to interpret the result, namely, in the case of carvacrol and thymol, which have the following rotations.

	Mol. rot.	Diff.
Carvacrol....................	16·313	0·193
Thymol......................	16·120	

The positions in the former are $CH_3 : OH : C_3H_7 = 1 : 3 : 4$, whereas in the latter they are as $CH_3 : OH : C_3H_7 = 1 : 2 : 4$. So that in carvacrol the hydroxyl is meta- to the methyl and ortho- to the propyl, and in thymol the hydroxyl is ortho- to the methyl and meta- to the propyl. The question is which of these hydrocarbon radicles should be taken as holding the position of reference. The rotations, however, are seen to vary, though the difference between them is of a somewhat indefinite kind, being rather too small if they are related as ortho- and meta-.

Amongst the ethereal salts of the benzenedicarboxylic acids, there is one inconsistency which it is difficult to understand, thus

	Mol. rot.	Diff.
(Ortho) Ethylic phthalate......	16·909	−0·792
(Para) „ terephthalic ...	16·117	+0·825
(Meta) „ isophthalic	16·942	

The difference between the ortho- and para-compounds shows the ortho- to have the higher rotation as usual, although it is larger than is generally found; the especially exceptional feature, however, is the meta-compound, in which the rotation is as high as that of the ortho-compound. The cause of this is very obscure, and must be due to some secondary influence.

Before passing from the subject of relative position, it is of interest to see how the compounds, whose rotations are influenced by it, compare with phenyl compounds in which it does not exist. Thus, for example, how the toluidines are related to aniline, the cresols to phenol, &c. In the following list, the rotations of the phenyl compounds are subtracted from those of similar substances differing in composition by CH_2, so that those which show the usual variation of rotation for this difference evidently must have rotations of a kind similar to those of the phenyl compounds. The difference given is that resulting from the subtraction of the rotation of the substance at the bottom of each set from that of *each* of those above it.

	Mol. rot.	Diff. for CH_2.
Metatoluidine............	16·210	0·134
Paratoluidine............	16·188	0·112
Orthotoluidine...........	17·200	1·124
Aniline.............	16·076	
Metacresol..............	12·776	0·636
Paracresol...............	12·869	0·729
Orthocresol..............	13·382	1·242
Phenol..............	12·140	
Metatolyl methyl oxide ..	14·646	0·688
Paratolyl ,, ,, ..	14·712	0·754
Orthotolyl ,, ,, ..	15·190	1·242
Phenyl methyl oxide..	13·958	
Parachlorotoluene........	13·246	0·736
Orthochlorotoluene.......	13·719	1·209
Chlorobenzene.......	12·510	
Parabromotoluene........	15·167	0·661
Orthobromotoluidine......	15·674	1·178
Bromobenzene.......	14·506	

	Mol. rot.	Diff. for CH_2.
Paraxylene	12·810	0·653
Orthoxylene	13·345	1·188
Toluene	12·157	
Ethylic paratoluate	14·744	0·890
„ orthotoluate	15·065	1·211
„ benzoate	13·854	

From these comparisons, it is evident that ortho-compounds differ from the corresponding phenyl compounds by from 1·178 to 1·242, the average being 1·210 for difference of composition by CH_2 (excluding that of orthotoluidine, 1·124), whilst, for the para-, the differences are, again omitting that of toluidine, from 0·653 to 0·890, and the meta-, which agree closely, average 0·662. On referring to p. 1077, it will be seen that the difference between ethylic benzoate and α-toluate, namely 1·128 for CH_2, is very similar to that between aniline and orthotoluidine; between toluene and ethylbenzene 1·257; and between the phenyl methyl and ethyl oxides, 1·171; so that these differences are very similar to those between phenyl compounds and the corresponding ortho-compounds containing one CH_2 more. From this it is evident that, in their rotation, ortho-compounds agree closely with phenyl compounds.

II. *The α- and β-positions in the Naphthalene Series.*

The following are two sets of comparisons.

	Mol. rot.	Diff.
α-Naphthyl ethyl oxide	32·237	1·539
β-Naphthyl ethyl oxide	30·698	
α-Naphthylamine	37·478	1·778
β-Naphthylamine	35·700	

These differences show that the α-compound compares with the ortho- in the benzene series, inasmuch as it is higher in rotation than the β-compound. The differences, however, are between two and three times as large, and, as in the case of the ortho- and paratoluidines, the naphthylamines show the largest difference.

Irregularities in the Rotation of some Methylated Phenolic Compounds, also of some Toluene and Naphthalene Derivatives of the Dimethyltoluidines and Dimethylnaphthylamines.

The number of substances which do not seem to behave normally in respect to position is probably less than appears at first sight, because one abnormal product, if used as a standard for reference, makes those compared with it appear exceptional, as will be seen from the following considerations.

In Table VI (p. 1127), it is seen that the derivatives of pyrocatechol and homopyrocatechol do not differ very much in respect to their methyl displacement; being dihydroxybenzenes, it is not likely that they should behave in quite the same manner as the monhydroxy-compounds. In the case of pyrocatechol, they stand to each other thus.

	Mol. rot.	Diff.
Veratrol	16·837	
Guaiacol	14·687	2·150
Pyrocatechol	13·022	1·665
Average		1·907

From this, it appears that the hydrogens of the different hydroxyls displaced give different numbers.

In the case of homopyrocatechol, the separate substances with these different displacements have also been examined, and we get

	Mol. rot.	Diff.
Dimethylhomopyrocatechol	17·484	
Creosol	15·405	2·079
Homopyrocatechol	13·306	2·099
Average		2·089

Considering that these compounds are not quite comparable, there is a fairly close analogy, and it is worthy of notice that the average result for the influence of methylation in these cases is only a little more than that of mono-displacements in the ordinary phenols, namely, about 1·800.

The effect of methylation on resorcinol is, however, anomalous, as the rotation is increased by a much smaller amount than in the above cases, namely, by 1·411; therefore, if dimethylresorcinol were used as a substance for reference in connection with the methylated orthodihydroxybenzenes, an unusually large difference would be found, and this would be misleading.

A similar kind of anomaly to the above occurs in the case of salicylaldehyde, and apparently also in salicylic alcohol (saligenin), the increase of rotation for one methyl being only 0·901, or about that usually found in the fatty series; this is unexpected, because, in the closely allied compound, ethylic salicylate, it amounts to 1·790, or about the usual amount for monhydroxy-derivatives, though the group $-COOC_2H_5$ is, no doubt, of a more rigid character than that of COH, or even $-CH_2 \cdot OH$.

With respect to the methylation of trimethylpyrogallol, the influence of the methyl groups is also very small, and its rotation apparently abnormal.

In some of these low-rotating methylic compounds, it is most likely that the oxygen has taken the ketonic condition, and the methyl is united with an adjacent carbon group, in the manner referred to on p. 1140; it is also probable that some may be mixtures of this with the normal form of methylated compounds.

Instances of an opposite character to the above, in which the rotation is high, occur in the case of some para-compounds; dimethylquinol, for example, when compared with the ortho-compound, veratrol, appears to have a higher rotation than would be expected, the former being only 0·125 lower than the latter, instead of about 0·517.

But the most marked examples are those of anisaldehyde and ethylic anisate. From Table VIII (p. 1128) it will be seen that the aldehyde has a rotation of 1·170, and the ethereal salt of 0·735, higher than they should have according to the ordinary relationships (the refractive power of ethylic anisate is also high), whilst anisic alcohol (prepared from the aldehyde by means of caustic alkali), gives a rotation which is about normal.

It is unfortunate that neither the ethylic nor the methylic salts of parahydroxybenzoic acid, or of parahydroxybenzaldehyde, lend themselves to measurement, otherwise we might be able to ascertain whether any peculiarities exist in their rotations, or whether those found in their methylic derivatives are due solely to methylation. From the very high numbers obtained, it appears likely that the initial substances are exceptional in character, and, if so, this would point to the probable existence of two varieties of parahydroxybenzoic derivatives, although at present it cannot be seen how this is possible. There is, however, one matter worth referring to in connection with this view. It has been seen that anisic alcohol (prepared from the aldehyde by the action of alkali) behaves normally; now this, according to Cannizzaro, fuses at 25°. A specimen of my own preparation, purified by thorough draining on a porous plate, melted at 21—21·5°, but Biedermann (*Ber.*, 1886, **19**, 2375), who prepared parahydroxybenzoic alcohol from parahydroxybenzaldehyde by the action of nascent hydrogen, obtained, by methylation of the product, an anisic alcohol, having a fusing point of 45°, so that, unless there is some mistake with regard to the latter, it would appear that two anisic alcohols exist.

Another exception, similar to that of ethylic anisate, is found in the case of ethylic α-naphthoate, which, however, cannot be due to methylation, thus

	Mol. rot.	Diff.
α-Ethylic naphthoate........	27·161	− 0·200
β-Ethylic naphthoate........	27·361	

In this comparison, the β-compound, which should correspond to a meta- or para-derivative, has a higher rotation than the α-compound, instead of being about 1·54 lower. (The refractive powers of these compounds are also in agreement with their rotations.)

The corresponding comparison of ethylic methysalicylate and the anisate give—

	Mol. rot.	Diff.
Ethylic methylsalicylate	17·156	− 0·129
Ethylic anisate	17·285	

Most remarkable parallel anomalies are found in the toluene and naphthalene series, in connection with the nitriles and dimethylated monamines.

Taking the nitriles first (the ortho- and α-compounds being apparently normal), the comparisons give—

	Mol. rot.	Diff.
Orthotoluonitrile	12·980	− 0·019
Paratoluonitrile............	12·999	
α-Naphthonitrile	24·788	− 1·476
β-Naphthonitrile	26·264	

In both these sets of comparisons, the differences vary in a similar manner, although to a different degree, those connected with the naphthalene compounds being by far the largest, as might be expected.

It would have been anticipated, however, that the paranitrile would have had a rotation about 0·52 smaller than the ortho-derivative, instead of which it is practically the same, whilst the β-nitrile should have a smaller rotation than that of the α-compound by about 1·50.

These nitriles, however, although analogous in their rotations, differ somewhat in their properties, those of the toluene series yielding ortho- and para-toluic acids, the ethereal salts of which give rotations showing the ordinary kind of difference between ortho- and para-compounds, though rather smaller. The naphthonitriles, on the other hand, give acids, the ethereal salts of which, as seen above, yield an abnormal difference of the same character as the nitriles, though smaller, so that in this case the peculiarity of character follows on from the nitriles to the acids.

Of all the results which have as yet been obtained, the most remarkable are those in connection with the dimethylated toluidines and naphthylamines. Their peculiarities have already been referred to (p. 1108).

Before considering their rotations it may be of interest first to refer to their boiling points.

The effect of dimethylation on aniline is to increase the boiling point 9°. In the case of paratoluidine, the increase is rather larger, namely, 10·9°, but with orthotoluidine there is a *reduction* of boiling point of no less than 14°, whilst on comparing the dimethyl derivatives it is found that dimethylorthotoluidine boils 25·7° lower than dimethylparatoluidine.

The difference in the boiling point of α- and β-napthylamine is 5·3° (at 760 mm.), the latter being the higher of the two; but α-dimethylnaphthylamine boils 28° *lower* than β-dimethylnaphthylamine (both under a pressure of 69 mm.) the relationship being similar, but larger than in the case of the dimethylated toluidines. These differences are very remarkable.

In the following table the rotations and differences are given, and also the rotations calculated on the assumption that the substances would give normal results, the para-compounds being taken as of the normal kind, which is borne out by analogy, the β-naphthalene compounds which represent either the para- or meta-derivatives being regarded from the same point of view.

	Mol. rot.	Diff.	Expected rot.	Diff.
Dimethylparatoluidine........	22·842	—	22·842	0·000
Paratoluidine................	16·188	6·654	—	—
Dimethylorthotoluidine	18·617	—	23·695	5·078
Orthotoluidine	17·200	1·417	—	—
Dimethyl-β-naphthylamine	47·377	—	47·377	0·000
β-Naphthylamine	35·700	11·677	—	—
Dimethyl-α-naphthylamine	35·994	—	49·155	13·161
α-Naphthylamine.............	37·478	−1·484	—	—

From this it is seen that the influence of methylation only raises the rotation in the case of orthotoluidine less than a fourth as much as it does in paratoluidine, in fact, rather less than it would in the fatty series, and, therefore, a slight reduction occurs. The rotation is also seen to be 5·078 less than might be expected. In the case of the α-naphthylamine compounds, the rotation has actually been diminished by 1·484 by methylation, and the result is 13·161 lower than anticipated.

The effect of saturation on the nitrogen of the dimethyltoluidines by converting them into hydrochlorides was tried, and the result was again very remarkable, thus:

Hydrochloride of dimethylorthotoluidine	18·705
,, dimethylparatoluidine	18·465
Diff. due to position....	0·240

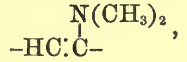
In these compounds it is seen that all the peculiarities of the bases have entirely passed away, and they are related in the same way as ordinary ortho- and para-compounds, except that the difference is slightly smaller than usual. No doubt similar results would be obtained with the two dimethylnaphthylamines.

Now, this change has come about by saturating the nitrogen. It would appear that the nitrogen is the active cause of the peculiarities of the free bases, but nitrogen as NH_2 does not cause these remarkable results until it is methylated and converted into $N(CH_3)_2$, probably the influence of the methyls may simply act as accentuating the properties of the nitrogen.

The rotations of orthodimethyltoluidine and dimethyl α-naphthylamine being so much lower than that of the corresponding para- and β-compounds, can only be explained on the assumption that they are less unsaturated. It will be seen further on (p. 1141) that as saturation increases, the rotation greatly diminishes, especially in the aromatic series.

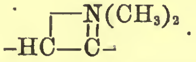
The low boiling points of these bases are also in agreement with this view, because saturated aromatic compounds, in most cases have lower boiling points than unsaturated.

For these bases to be less unsaturated than the corresponding para- and β-compounds, requires that the two valencies of the nitrogen which are usually free, should influence the carbon of the benzene ring; thus, taking a section of the latter, the relationships of these bases may be represented as follows.



$$-HC\colon\overset{\overset{\displaystyle N(CH_3)_2}{|}}{C}-\,,$$

Dimethylpara- and β-.



$$-HC—\overset{\overset{\displaystyle N(CH_3)_2}{\|}}{C}-\,.$$

Dimethylortho- and α-.

It is seen that this second arrangement must break down on the formation of a hydrochloride, and this is in agreement with the rotation.*

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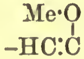
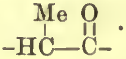
* If this condition of things exists in these bases, it might occur also in the rosaniline bases, and furnish an explanation why they are colourless in the free state but form coloured salts with acids, because the partial saturation of one of the nuclei would probably be quite enough to account for the colourless condition, whilst the formation of the salt would cause it to become normal, and thus possessed of colour.

This view is in many respects very similar to that which is believed to occur on methylating some hydroxy-compounds, where the normal and abnormal results are represented thus



$$\begin{array}{rl} & \text{Me·O} \\ & \quad\,| \\ \text{–HC:} & \!\!\text{C} \end{array}$$



$$\begin{array}{c} \text{Me}\;\;\text{O} \\ |\qquad\| \\ \text{–HC—C–} \end{array}$$

The above is not the only possible arrangement, another might be imagined in which the nitrogen remains only singly united to its original carbon, whilst its fourth and fifth valencies influence two other carbons of the nucleus.

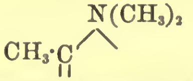
Some rough experiments were made in reference to the heat evolved on the union of ortho- and para-dimethyltoluidines with hydrochloric acid, because it appeared probable that if these internal saturations exist in the ortho-base, and are broken up on its union with an acid, the heat given off should differ in amount from that evolved by the para-base under the same circumstances. The result of the determinations was that with the ortho-base considerably more heat was evolved than with the para-base.

Similar experiments were made with ortho- and para-toluidine to see what difference position would make, and it was found that there was a slightly greater rise in the temperature with the para- than with the ortho-compound, or the reverse of that found with the methylated compounds.

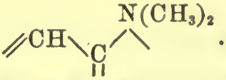
The acid used was strong (26 per cent.) and in the proportion of four to one of base for the methylated compounds, but much more dilute for the toluidines. Para-toluidine being solid was examined in solution in its own weight of orthotoluidine.

These experiments were made side by side but without taking any special precautions, still the indications they furnish seem to be of sufficient interest to make it desirable to further investigate this subject.

Another question of interest is, why should the orthotoluene and β-naphthalene compounds behave in an analogous manner; what is there in common between them? The only point of resemblance is that a carbon ortho- to the –CN or $N(CH_3)_2$ groups in both cases is in union with a second carbon group, thus



In dimethyl-orthotoluidine.



In dimethyl-α-naphthylamine.

Unsaturated Compounds and Influence of Stereoisomerism.

The substances referred to under this heading consist of benzenoid compounds, with side chains containing an unsaturated group. They are of *two* classes, namely, those in which the unsaturated group is indirectly attached to the benzene nucleus by intervening saturated carbon groups or oxygen, and those in which it is directly united. The former will be considered first.

Class I.

Allylic Benzoate.—The following is a comparison of the rotation of this substance with its representative containing a saturated chain.

	Mol. rot.
Allylic benzoate	15·722
Propylic benzoate	14·873
Diff. for unsaturation by $-H_2$..	0·849

This difference, though rather smaller, is similar to that found in other allyl displacements; in the fatty series, those found for allylacetic acid and ethylic allylmalonate are 0·918 and 0·914 respectively. The comparisons, however, are not quite of the same kind, as these products are allyl displacements in the acid radicles, and not allylic salts. In allylic benzoate, the screening between the nucleus and the unsaturated group is extensive, and probably quite enough to entirely stop the one from influencing the other. It consists of $-CO{\cdot}O{\cdot}CH_2-$, thus

$$\text{Allylic benzoate} = C_6H_5|CO{\cdot}O{\cdot}CH_2|CH{:}CH_2.$$

Phenyl Allyl Oxide.

Compared in a similar manner to the previous substance it gives

	Mol. rot.
Phenyl allyl oxide	17·134
Phenyl propyl oxide...........	16·187
Diff. for unsaturation by $-H_2$	0·947

This difference is a trifle higher than that given in the foregoing case just referred to. This might be expected, because the groups are not of so effective a screening character as in allylic benzoate, consisting only of $-O{\cdot}CH_2-$, thus

$$\text{Phenyl allyl oxide} = C_6H_5 \mid O{\cdot}CH_2 \mid CH{:}CH_2.$$

Paratolyl Allyl Oxide.

The compounds containing saturated chains and corresponding to this and the next substance have not been examined; therefore, to study the rotation of these it will be necessary to find the value of the allyl group, as nearly as possible, because if this resembles that found in fatty compounds, the difference for unsaturation must also be similar. In the case of paratolyl allyl oxide this can be done by comparing it with paratolyl methyl oxide, and allowing for the CH_2 in excess due to the methyl. (Comparisons with paracresol would not be suitable.)

	Mol. rot.
Paratolyl allyl oxide	17·571
Paratolyl methyl oxide $-CH_2$ (14·712—1·037)....	13·675
Allyl disp. H	3·896

In allylacetic acid and ethylic allylmalonate, the value for allyl displacing hydrogen is 3·871 and 3·901 respectively. The screening here is the same as in the previous example of phenyl allyl oxide, namely, $-O{\cdot}CH_2-$, thus

Paratolyl allyl oxide .... $CH_3{\cdot}C_6H_4 \mid OCH_2 \mid CH{:}CH_2$.

Eugenol.—The substance most nearly related to this which has been measured is guaiacol, the former being a para-allyl derivative of this compound. The rotations of these two substances are

	Mol. rot.
Eugenol	18·727
Guaiacol	14·689
Allyl disp. H......	4·038

The difference between these rotations for allyl displacing hydrogen is analogous to that found in the fatty series but a little higher. There is a defect in the above comparison, because the displacement of hydrogen by allyl, in the *para* position, is not likely to be the same as it would be in a benzene compound where relative positions do not exist; in fact it would probably be lower, so that the above number is too high rather than too low, and simply due to the screening influence of CH_2 being less than that of the oxygenated groups in the previous examples. The following shows its position.

$O{\cdot}CH_3(OH)C_6H_3 \mid CH_2 \mid CH{:}CH_2$.

So that in the cases of allylic benzoate, paratolyl allyl oxide, and eugenol, some idea of the influence of the groups, $-CO{\cdot}O{\cdot}CH_2-$, $O{\cdot}CH_2-$, and CH_2, when screening off the $-CH{:}CH-$ from the nucleus, the first being the most perfect, the second less so, and the third the least of the three.

The relationship of eugenol to isoeugenol is considered further on.

Class II.—Cinnamene, Allylbenzene, and Butenylbenzene.

These three hydrocarbons are more closely related than their names indicate. Cinnamene may be regarded either as phenylvinyl, or phenylethylene, the others being methyl derivatives of this compound. This will be seen from the following table, which also gives their molecular rotations and their differences.

Substance.	Mol. rot.	Diff. for CH_3 disp. H.
Cinnamene, phenylethylene, $C_6H_5{\cdot}CH{:}CH_2$	16·041	
		1·558
Allylbenzene, phenylmethylethylene, $C_6H_5{\cdot}CH{:}CH{\cdot}CH_3$	17·599	
		0·763
β-Butenylbenzene, phenyldimethylethylene, $C_6H_5{\cdot}CH{:}C(CH_3)_2$	18·362	
	Average..	1·112

In this series, the first displacement of hydrogen by methyl increases the rotation more than would be expected by the change of composition; this is probably due to the influence of the phenyl and the unsaturated group. The second result being smaller may be because the amount of influence is spread over both methyls, so that in the dimethyl compound the methyls would have the average values of 1·112.

These hydrocarbons when compared with their representatives with saturated chains give

Substance.	Mol. rot. 15°.	Diff. for unsaturation by $-H_2$.
Cinnamene	16·041	2·627
Ethylbenzene	13·414	
Allylbenzene	17·599	3·046
Propylbenzene	14·553	
β-Butenylbenzene	18·362	2·732
Butylbenzene (calc.)	15·630	
Average		2·834*

From these examples, it is seen how much more the unsaturated group affects the rotation when in *direct* union with the benzene nucleus than it does when the intervening groups $CO{\cdot}O{\cdot}CH_2$, $-O{\cdot}CH_2-$, or $-CH_2-$ separate them, being more than three times as great as when this is the case, as in Class I. In the fatty series, the effect of unsaturation is not always quite the same; as already mentioned, in allyl compounds it is about 0·918, but in most others its average value is about 1·112, so that it is not surprising to find it fluctuate also in the above hydrocarbons and other aromatic compounds.

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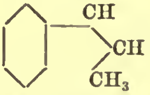
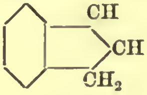
[*] These numbers vary a little from those already given (Trans., 1892, **61**, 830), owing to the averaging in of fresh determinations and calculating the results as a whole, instead of taking averages of various determinations. This will apply to some other numbers already published.

Indene Synthetical.—This does not strictly belong to this class of hydrocarbons, but it is convenient to refer to it here on account of its relationship to allylbenzene, which may be seen from the following,



Allylbenzene.



Indene.

The difference between indene and hydrindene is small for the variation in composition of H_2. It is as follows

	Mol. rot.
Indene	16·202
Hydrindene	13·928
Diff. for H_2..	2·274

On reference to the above table, it will be seen that if the comparison were strictly correct, which it is not since it refers to a ring compound, it would be about 2·834 in the case of hydrindene. Nevertheless, it would seem that the CH_3 group attached to the nucleus in this manner weakens the influence of the unsaturated group, and it is interesting to notice that the effect of the conversion of allylbenzene into indene by loss of H_2 is actually attended with lowering of the rotation, through the free end of the chain forming a second junction with the benzene ring. The following comparisons show the difference

	Mol. rot.
Allylbenzene	17·596
Indene	16·202
	1·394

That this kind of junction, with loss of H_2, even when no saturated group is present, does not act on the rotation to such an extent as that of ordinary unsaturation by loss of H_2, is seen by comparing dibenzyl, stilbene, and phenanthrene, the difference between the first two being more than twice as great as that between the last two (see pp. 1150, 1151).

In most of the following examples of substances connected with the second class, another influence has to be taken into account when considering that of unsaturation, namely, *stereoisomerism*, such as is found in relation to maleic and fumaric acids, and it may be well, therefore, to consider this before proceeding further.

The only two isomeric substances of the same constitution in the aromatic series, which differ from each other in this respect only, and which have been measured, are the methylic salts of α- and β-orthomethoxyphenylacrylic acids, coumarin being the starting point for the preparation of the first, and methylsalicylic aldehyde for the second (Trans., 1877, i, 414, 417, &c.); in fact it was with a hope of getting some clue to the variations between these substances that I originally commenced the study of the magnetic rotation of compounds. The formula for these methylic salts is

$$CH_3O{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}OCH_3.$$

Their rotations are

	Mol. rot.
Methylic β-orthomethoxyphenylacrylate	22·359
,, α-orthomethoxyphenylacrylate	21·891
Difference................	0·468

This difference is very similar to that existing between the rotation of the ethylic salts of fumaric acid and maleic acid, which is 0·487 (Trans., 1888, **53**, 601). It is well to bear in mind that this amount varies in the case of the compounds of the fatty series (being 0·716 between the ethylic salts of mesaconic and citraconic acids, the highest result observed), and in like manner it may not always be the same in the aromatic series. The *trans* or fumaroid compound has always the largest and the abnormal rotation in both series.

Cinnamic Compounds.

In the following table, the rotations of the compounds of this series which have as yet been measured are compared with those of their representatives with saturated side chains.

	Mol. rot.	Diff. for unsaturation by $-H_2$.
Ethylic cinnamate........	20·006	3·837
,, hydrocinnamate...	16·169	
Cinnamaldehyde	17·885	3·724
Hydrocinnamaldehyde*...	14·161	
Cinnamic alcohol	17·940	3·225
Hydrocinnamic alcohol*..	14·715	
Cinnamic ketone (benzylidene acetone)	19·235	4·323
Hydrocinnamic ketone* ..	14·912	

These results are in all cases, except that of cinnamic alcohol much higher than the difference for unsaturation of the hydrocarbons (2·834); that the rotation of the alcohol is also somewhat above this amount is probably due to the difference for unsaturation in this series being slightly higher than that of the hydrocarbons. The largeness of the results obtained with ethylic cinnamate and cinnamic aldehyde is no doubt due to these compounds being of a *fumaroid* character, because if the variation in rotation due to this influence, as found between the α- and β-methylic orthomethoxyphenylacrylates (0·468), be subtracted from these differences, the remainder is nearly the same as that found for cinnamic alcohol, thus

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* These numbers were obtained by adding the difference for C_2H_4 found between ethylic benzoate and hydrocinnamate, namely 2·315, to benzaldehyde, benzylic alcohol and acetophenone respectively.

Diff. for ethylic cinnamate	3·837
Less diff. for stereoisomerism	0·468
Diff. for unsaturation by $-H_2$	3·369
Diff. for cinnamaldehyde	3·724
Less diff. for stereoisomerism	0·468
Diff. for unsaturation by $-H_2$	3·256
Diff. for cinnamic alcohol for unsaturation only	3·225
Average	3·287

These results are interesting, because they show not only that ethylic cinnamate, in accordance with the researches of Liebermann, is a *fumaroid* compound, but also that cinnamic aldehyde is of this nature, and at the same time they indicate that cinnamic alcohol is a *normal* compound.

Again, with respect to unsaturation, these compounds all show how extremely large the effect of this is when the unsaturated group is in direct union with the benzene nucleus, averaging, in these cases, 3·287.

In passing, it may be as well to remark that as cinnamic acid and orthomethoxyphenylacrylic acid (that is, methylcoumaric acid), which are prepared from benzaldehyde and methylsalicyaldehyde, by means of acetic anhydride and sodium acetate, are both *fumaroid* compounds, probably all the acids produced from the aromatic aldehydes by this method are compounds of this description.

Cinnamyl Methyl Ketone (Benzylidene-acetone),

$$C_6H_5\cdot CH{:}CH\cdot CO\cdot CH_3.$$

The difference between this compound and its saturated representative, as seen in the foregoing table, is very high, and it is difficult to be sure of the real cause, as three different influences may be connected with it. The chief, no doubt, is unsaturation, and probably is similar in amount to what it is in the other cinnamic compounds, namely, 3·287, but this leaves 1·036 to be accounted for; this may be due to either one or two causes, that is to say, it may result solely from the presence of a certain amount of a tautomeric form of the ketone, or to this combined with stereoisomerism. The existence of the first influence might perhaps be detected by measuring the rotation at temperatures wide apart, and ascertaining whether it changes materially, as is usual with tautomeric compounds of this class, but at present this has not been done. There can be no doubt, however, as to this substance having at least the same difference for unsaturation as the other products related to it.

Methylic α- and β-Orthomethoxyphenylacrylates.—The difference between these two substances in respect to stereoisomerism has been considered, but nothing has been observed in reference to the consistency or otherwise of their rotation when compared with that of other related compounds, the means for comparison unfortunately not being very good. Taking the β- or *fumaroid*-compound, it represents ordinary methylic cinnamate with hydrogen displaced by CH_3O in the *ortho*-position. Methylic cinnamate has not been measured, but if it be assumed that it differs from the ethereal salt in the same way as methylic benzoate differs from its ethereal salt, namely, by 1·111, the rotation will be 18·895, and if to this the value of CH_3O in the ortho-position of a hydroxy-acid, be added (found by subtracting the rotation of ethylic benzoate from that of ethylic methylsalicylate), namely, 3·302, 22·197 is obtained for the rotation, 22·359 having been found. This is as close as could be expected from such an estimate, where all the differences used in the comparisons are taken from a series varying by $+H_2$. The rotation of this compound may therefore be considered consistent with that of cinnamic acid. The rotation of the α-compound is also in agreement with this, because it simply differs, as before shown, from the β-compound in the same way that ethylic maleate does from ethylic fumarate.

Isoeugenol.—This is a very interesting compound, because, when compared with eugenol, it shows how greatly substances of Class I and Class II differ. The difference of structure of these compounds is as follows

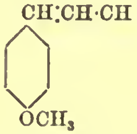
Eugenol, $OCH_3{\cdot}C_6H_3(OH){\cdot}CH_2{\cdot}CH{:}CH_2$,
Isoeugenol, $OCH_3{\cdot}C_6H_3(OH){\cdot}CH{:}CH{\cdot}CH_3$.

the unsaturated group being separated from the nucleus by CH_2 in the former case, whereas it is in union with it in the latter.

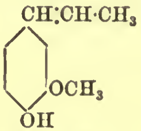
The comparison of their rotations shows what the difference due to the screening influence of CH_2 amounts to in this case.

	Mol. rot.	Diff.
Isoeugenol	21·469	2·742
Eugenol	18·727	

Anethole.—This being a derivative of methylparahydroxyphenylcrotonic acid, which is a *fumaroid* compound, is, no doubt, also a compound of this character. It is also closely related to isoeugenol, thus



Anethole.



Isoeugenol.

the one substance being a methylated derivative of a monhydroxyphenol, and the other a monomethylated derivative of a dihydroxyphenol.

After subtracting the amount due to the *fumaroid* condition from the rotation of anisoïl, it may be compared with that of isoeugenol, and will then show to what extent they vary for the difference of OH in their composition.

	Mol. rot.
Isoeugenol	21·469
Anethole, 21·089 − 0·468	20·621
Diff. for OH....	0·848

Substitutions in the para- and meta-positions are not usually very different in their effect on the rotation, so that a rough estimate of what this difference should be is obtained by subtracting the rotation of toluene from that of paracresol, thus

$$12·869 - 12·157 = 0·712.$$

This is not far from the above.

It is interesting to compare this compound with its isomer, allyl paracresyl oxide.

	Mol. rot.
Anethole, less fumaroïd influence....	20·621
Paratolyl allyl oxide	17·571
	3·050

This gives much the same kind of difference, but, as might be expected, rather larger than that found between isoeugenol and eugenol (2·742), because the unsaturated group, –CH:CH–, in paratolyl allyl oxide is separated from the nucleus, not only by CH$_2$, as in eugenol, but also by oxygen; thus the screening influence is greater, and consequently the rotation is lower.

To estimate the rotation which complex aromatic substances should have, by calculation from that of some allied compound and the differences found in relation to other substances, must in many cases be more or less inaccurate; nevertheless, it has proved very useful in numerous instances, as it is important to test the magnetic rotation and see if this property varies consistently.

The following is one of the methods which can be used in the case of anethole.

	Mol. rot.
Allylbenzene, $C_6H_5\cdot CH{:}CH\cdot CH_3$	17·599
Influence of OCH_3 as found in paratolyl methyl oxide	2·555
	20·154
Difference for *fumaroid* condition	0·468
Anethole	20·622

It is seen that this does not vary very greatly from that found for anethole (21·089), though it is rather low. This, however, may arise, at least in part, from the estimate for the OCH_3 being too low, as it has been noticed that in para-methylated substances, such as dimethylquinol, this does not always appear to act regularly when in this position.

In reference to the unsaturated compounds of Class II, there is a remarkable point worth noticing in relation to their rotations, and that is, that the effect of the introduction of the group $-CH{:}CH-$ on their rotation increases the latter to a greater extent than the influence this group exerts in benzene itself (3·761).

In the following comparison, the difference for the *fumaroid* condition has been subtracted from the rotations of ethylic cinnamate and cinnamaldehyde.

Substance.	Formula.	Mol. rot.	Diff. for $-CH{:}CH-$.
Cinnamene	$C_6H_5\cdot CH{:}CH\cdot H$	16·041	4·757
Benzene	$C_6H_5\text{———}H$	11·284	
Allylbenzene	$C_6H_5\cdot CH{:}CH\cdot CH_3$	17·599	5·442
Toluene	$C_6H_5\text{———}CH_3$	12·157	
Ethylic cinnamate	$C_6H_5\cdot CH{:}CH\cdot CO\cdot O\cdot C_2H_5$	19·538	5·684
Ethylic benzoate	$C_6H_5\text{———}COOC_2H_5$	13·854	
Cinnamaldehyde	$C_6H_5CH{:}CH\cdot CO\cdot H$	17·417	5·553
Benzaldehyde	$C_6H_5\text{———}CO\cdot H$	11·864	
Cinnamic alcohol	$C_6H_5\cdot CH{:}CH\cdot CH_2OH$	17·940	5·540
Benzylic alcohol	$C_6H_5\text{———}CH_2OH$	12·400	

The average of the last four differences is 5·555; the first comparison is with benzene itself, and not with a displacement compound of the hydrocarbon as in all the other cases, and gives a difference which would not be suitable to take into the general average; but although not quite so large as the other numbers, it is still much larger than that given above for –CH:CH– in benzene.

Seeing that the unsaturated group attached to the benzene nucleus is, in the above compounds, only a part of a side chain, it is difficult to imagine that its rotation can be actually larger than it is when forming part of the benzene ring. The only conclusion that can be come to is that its presence exerts an augmenting effect on the rotation of the nucleus. It has already been seen that whenever a –CH_2– group enters the nucleus the rotation is increased more than is required by the change of composition; this, therefore, makes it appear the less strange, that when united with unsaturated groups of the same kind as those it is composed of, they should influence the rotation still more.

In the foregoing examples, the unsaturated chain is united on one side with a benzene nucleus, and on the other with a saturated group; it is of interest, therefore, to see what is the effect of uniting both sides with benzene nuclei. This occurs in the case of stilbene, and a comparison of the rotation of this with twice the value of C_6H_6 less H_2, will give the result, thus

	Mol. rot.
Stilbene	33·143
$C_6H_6 \times 2$ less H_2	22·060
Influence of –CH:CH– ..	11·083

This shows that its effect has been more than doubled.

The difference between stilbene and dibenzyl is also interesting, as it gives simply the effect of unsaturation.

	Mol. rot.
Stilbene	33·143
Dibenzyl	24·977
Diff. for unsaturation by $-H_2$..	8·166

This is a very remarkable result, showing clearly that the influence of the group –CH:CH– evidently spreads over both the nuclei with which it unites, its effect being at the same time more than doubled.

A comparison of the effects of this group when entering compounds under the following conditions, is interesting.

Between two saturated groups..........	3·127*
„ one saturated and one benzene group	5·555
„ two benzene groups	11·083

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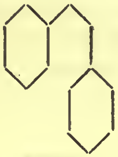
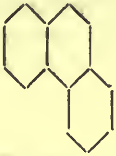
* Rotation of ethylic α-crotonate less than that of ethylic acetate, 7·589 − 4·462 = 3·127.

The relationships and the change in rotation which occurs when stilbene becomes phenanthrene by loss of H_2 is as follows.



Stilbene.



Phenanthrene.

	Mol. rot.
Phenanthrene	36·959
Stilbene	33·143
	3·816

This result is not so large as might at first sight be anticipated, but it does not represent a change of ordinary unsaturation, although there is a separation of H_2, because in this case the loss is attended by recombination to form a third condensed nucleus.

Looking at the hydrocarbons which have been examined, simply with respect to their composition, it might be thought that some relationship should exist between them relatively to the degree of unsaturation they *appear* to have. The following list has been compiled with this object.

Toluene	C_nH_{2n-6}	C_7H_8	12·157
Allylbenzene	C_nH_{2n-8}	C_9H_{10}	17·599
Hydrindene	,,	C_9H_{10}	13·928
Indene	C_nH_{2n-10}	C_9H_8	16·202
Naphthalene	C_nH_{2n-12}	$C_{10}H_8$	25·125
Diphenyl	C_nH_{2n-14}	$C_{12}H_{10}$	25·304
Acenaphthene	,,	$C_{12}H_{10}$	28·636
Diphenylmethane	,,	$C_{13}H_{12}$	23·845
Dibenzyl	,,	$C_{14}H_{14}$	24·977
Stilbene	C_nH_{2n-16}	$C_{14}H_{12}$	33·143
Phenanthrene	C_nH_{2n-18}	$C_{14}H_{10}$	36·959
Triphenylmethane	C_nH_{2n-22}	$C_{19}H_{16}$	36·011

Although the above rotations can only be compared in a general way, on account of the varying composition of the substances they represent, yet it is obvious that they do not, except in the cases of dibenzyl and stilbene, follow in any definite order.

Taking, for example, the isomeric substances, allybenzene and hydrindene; diphenyl, and acenaphthene, it is seen that their rotations differ largely. Although naphthalene appears in this list as a $2n-10$ compound, containing C_2H_2 less than diphenyl, which is represented as a $2n-14$ compound, it has nearly the same rotation. Again, phenanthrene when compared with triphenylmethane, from which it differs by C_5H_6, and also very largely in apparent unsaturation ($2n-18$ to $2n-22$), yet has the higher rotation.

This shows how greatly magnetic rotations are influenced by the arrangement of the molecules in the compound, and not simply by their composition.

SECTION IV.—REFRACTIVE POWER OF AROMATIC COMPOUNDS.

Owing to the analogies which have been found to exist between the magnetic rotation and refraction of substances, chiefly those of the fatty series, it was of interest to extend the inquiry to some of the questions connected with this paper, especially those relating to products belonging to the aromatic series.

Up to the present no critical experiments have been made in connection with the refractive power of mixtures, regarded from the same point of view as their magnetic rotation described in the early part of this paper; I hope, however, to study this subject shortly.

With respect to the influence of variation of temperature on the refractive power, this has already been shown to be of the same kind as that found for magnetic rotations (Trans., 1892, **61**, 187, 1896). An additional result has, however, been obtained in connection with this subject, namely, the temperature difference of dimethyl-α-naphthylamine, which amounts to 0·527 for 100° for the D-line. This is the highest yet obtained, α-naphthylamine giving the next highest, 0·466.

The points connected with the relationships holding amongst the ethylic salts of the aromatic acids, the mixed oxides, and most of the benzene hydrocarbons, have been discussed in relation to their rotation but have not yet been examined carefully in reference to their refractive power; the differences between the hydrocarbons for variation in composition by CH_2, however, do not seem to be normal.

The following are the principal subjects which have been considered.

Mono-, Di-, and Tri-phenylmethane.

Influence of the Phenyl Groups.

The molecular refractions of the following series of compounds, calculated for $\frac{\mu-1}{d}P$ and their differences, is given in the table.

	H_a.	Diff. for C_6H_5 disp. H.
Methane.................	10·200	
		41·815
Toluene, 99°	52·015	
		43·147
Diphenylmethane, 99°.....	95·162	
		43·857
Triphenylmethane, 99°	139·019	

Here, as in the rotation, the influence of the phenyl group increases considerably with each addition, and in the same order, the rate of increase being greatest between the first and second.

Diphenyl.

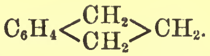
Direct Union of Phenyl Groups.

In the following comparison of diphenyl with benzene, it is necessary to correct the molecular refraction of the latter to 99° in order to make it comparable; for this the temperature coefficient of toluene must be employed, as that of benzene has not yet been determined. This reduces it to 43·749, twice this, less H_2, will be 85·898.

Diphenyl	90·088
Benzene × 2, less H	85·898
	4·190

This shows how much higher it is than in benzene, and, if divided by two, it gives 45·144 for C_6H_5, or 44·844 when it displaces H. This, it is seen, is higher than its influence in diphenylmethane and triphenylmethane as found in the case of the magnetic rotations.

Hydrindene (Synthetical),



$$C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>CH_2.$$

This has the same composition as xylene plus C. The relationships of the molecular refraction of these compounds are as follow.

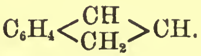
	Line A.	
Xylene (meta-) + C = 59·80 + 4·86	64·66	+0·19
Hydrindene	64·85	

These results show that hydrindene, apparently, has a molecular refraction which is about normal.

If compared with propylbenzene, less H_2, it gives

	Line H_α.	
Propylbenzene, 67·785* − 2·600....	65·185	+0·275
Hydrindene	65·460	

Indene (Synthetical),



$$C_6H_4<\begin{matrix}CH\\CH_2\end{matrix}>CH.$$

The difference between the molecular refraction of this and hydrindene is smaller than usual for the difference of composition by H_2, the latter being given by Brühl as 2·30 for H_α, and by Gladstone as 1·1 for A, thus

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* Calculated from the results of Landolt and Jahn (*Zeit. physikal. Chem.*, 1892, 10, 312).

	A.	H_α.
Indene	65·599	66·380
Hydrindene	64·850	65·460
	0·749	0·920

This is in accordance with the rotation, and is probably due to the same cause (see p. 1144). As might be expected, the dispersion of indene is evidently greater than that of hydrindene.

Phenylazoimide.

The following is a comparison of the refraction of this substance with that of benzene.

	Line A.
Phenylazoimide	59·421
Benzene	43·590
N_3 disp. H	15·831
H	1·300
N_3	3/17·131
N	5·710

This is higher than Gladstone's value for nitrogen in bases (5·1), and, therefore, the refractive power of this substance is in agreement with its magnetic rotation; probably the nitrogen in direct union with the nucleus has a larger influence than the others.

Monamines and Diamines.

Aniline, α- and β-Naphthylamine, and Metaphenylenediamine.

Influence of the NH_2 *Group displacing Hydrogen in Benzene and Naphthalene.*

It has long been observed that the refractive power of bases of the fatty series is relatively higher than that of other nitrogen compounds; so that a special value has been given for their nitrogen; it has also been known for some time that aniline and dimethylaniline have still higher refractive powers, and recently Brühl has published some interesting papers in reference to the peculiar behaviour of nitrogen compounds (*Zeit. physikal. Chem.*, 1895, **16**, 193, 226, 497, and 512).

The following are comparisons in connection with the general influence of the NH_2 group, mostly of a similar kind to those made in reference to the rotations.

	Line A.
Aniline	52·153
Benzene	43·590
NH_2 disp. H	8·563

The ordinary value of NH_2, displacing H in the fatty series, is only 6·4.

The same is found in the case of the toluidines, thus

	Line H_α.	NH_2 disp. H.
Orthotoluidine	60·658	8·332
Toluene	52·326	
Paratoluidine	60·708	8·382
Toluene	52·326	

In the case of the naphthylamines, still greater increases in the refractive power, due to this displacement, are found.

		Line H_α.	NH_2 disp. H.
α-Naphthylamine,	98·4°	85·469	9·359
Napththalene*	,,	76·110	
β-Naphthylamine	,,	86·670	10·560
Naphthalene	,,	76·110	

Metaphenylenediamine.

In the paraffin series, it appears that the second NH_2 introduced into the hydrocarbon has not quite so great an influence on its refractive power as the first, thus

	Line A.
Pentamethylenediamine (Trans., 1889, 750)	52·93
Amylamine (calc.)	46·77
NH_2 disp. H	6·16
The calculated difference is	6·4

The following are the results obtained with metaphenylenediamine.

	Line A.
Metaphenylenediamine	60·196
Benzene	43·590
Effect of $NH_2 \times 2$ disp. H_2	16·606
,, NH_2 disp. H in aniline	8·563
,, second NH_2 disp. H	8·043

As in the above case, this second displacement has a somewhat smaller effect than the first.

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* Nasini and Bernheimer (*Gazzetta*, 1885, **15**, 59).

All the above results are in agreement with the rotations, and show that in the refractive powers of these compounds the difference for NH_2 cannot represent values for this group, but rather the effect they produce on the molecule as a whole.

Derivatives of Monamines.

Dimethylaniline.

The effect of the methylation of aniline has already been referred to by Dr. Gladstone and myself (Trans., 1889, **55**, 755). The following comparisons show its influence.

	$\frac{\mu_A - 1}{d}p$.	CH_3 disp. H.
Aniline	52·153	8·297
Methylaniline	60·450	8·510
Dimethylaniline..........	68·960	

Effect of $CH_3 \times 2$ disp. H_2 .... 16·807

The ordinary increase is 15·2.

Here again there is a large increase above that which is usual, agreeing in this respect with the rotation, although of course it is not so large. There is another small point of difference in the rotation, the first difference being larger than the second, whereas in the refraction it is the reverse.

Dimethylortho- and Dimethylpara-toluidines and α- and β-Dimethylnaphthylamines.

In connection with these bases, which give such remarkable rotations, Brühl has already drawn attention to the anomalous refraction of dimethylorthotoluidine (*Zeit. physikal. Chem.*, 1895, **16**, 236).

His results for the dimethyltoluidines calculated for Gladstone's formula are as follows.

	H_α.	H_γ.
Dimethylparatoluidine	77·922	83·288
Dimethylorthotoluidine	73·791	80·037
	4·131	3·251

These show how very much lower the numbers are for the ortho-compound, and also that there is a considerable reduction in the dispersion. The ortho- should be slightly lower than the para-compound, as will be seen in the section on position, but this would only amount to a small fraction of the above. If the dimethyltoluidines be compared with the corresponding toluidines, the effect of the methylation will be clearly seen.

	Ortho- H_α.	Para- H_α.
Dimethyltoluidine	75·791	77·922
Toluidine	60·580	60·640
Diff. for $CH_3 \times 2$ disp. H_2.	15·211	17·282

The ordinary influence of $CH_3 \times 2$ disp. H_2 is 15·2, so that in the case of the ortho-compound the difference is practically the same as that found in the fatty series; this is inconsistent, because, as seen from dimethylaniline, it should be much larger. The difference for the para-compound is, however, analogous to that of dimethylaniline, although relatively rather higher.

With the dimethylnaphthylamines, the following results were obtained.

	t.	α-H_α.	t.	β-H_α.
Dimethylnaphthylamine ..	51·6°	100·641	53·2°	105·241
Naphthylamine	51·0	85·673	53·2	86·867
$CH_3 \times 2$ disp. H_2	—	14·968	—	18·374

Here the difference in reference to the α-compound is lower than that for the influence of $CH_3 \times 2$ disp. H_2 (15·2), whilst that of the β-compound is much above that found even in the case of dimethylparatoluidine.

The dispersion of the β-compound is also very much the higher of the two.

Disp. of α-dimethylnaphthylamine, $H_\gamma - H_\alpha$......	9·527
,, β-dimethylnaphthylamine, $H_\gamma - H_\alpha$......	13·294

All these results, therefore, are of the same character as those connected with the magnetic rotation, but whereas in orthodimethyltoluidine and dimethyl-α-naphthylamine, the differences for the methylation are approximately those found in the fatty series, in the rotations they are in the case of dimethyltoluidine less than in the fatty series, and in that of dimethyl-α-naphthylamine a *minus* quantity, the rotation being actually lower than that of α-naphthylamine itself.

Methyldiphenylamine and Benzylamine.

The molecular refractions of these isomeric bases are of interest, although of course they are not strictly comparable, one being a secondary and the other a tertiary compound, but this will not influence the comparison greatly.

	$\frac{\mu_A - 1}{d}p$.
Methyldiphenylamine	104·88
Benzylaniline	102·93
	1·95

This difference is chiefly due to the screening influence of the CH_2 group, between that of the nitrogen and one of the phenyls, and is in agreement with the rotation results.

Hydrochlorides of Monamines.

Dimethylaniline Hydrochloride.

As this salt was examined in the anhydrous state, and in a superfused condition, also in aqueous solution, it will be best to consider the numbers obtained with it first.

	H_α.	H_β.	H_γ.
Dimethylaniline hydrochloride, anhydrous	79·257	81·643	83·167
Dimethylaniline hydrochloride, solution ($C_8H_{11}N + 6·174H_2O$)	77·688	80·222	81·980
Influence of water	1·569	1·421	1·187

Unlike solutions of hydrochloric acid, and of lithium and sodium chlorides (Trans., 1891, **59**, 592, and 1895, **67**, 851), the effect of the water is to reduce the molecular refraction, just as it does the molecular rotation (Trans., 1889, **55**, 739, 742, &c.; 1894, **65**, 26, 27). It is interesting to notice that the dispersion of the solution is greater than that of the anhydrous salt.

The refractive power of the anhydrous salt is considerably less than that of the free base and hydrochloric acid, thus.

	H_α.
Dimethylaniline	69·865
Hydrochloric acid	11·170
	81·035
Found	79·257
Diff.	1·778

This loss is about the same as the remarkable increase above the usual influence for CH_3 disp. H, which occurs when aniline is converted into dimethylaniline, because it is found that the above value for the anhydrous hydrochloride is practically the same as that of aniline hydrochloride *plus* C_2H_4, thus.

	H_α.
Aniline	52·816
HCl	11·170
Aniline hydrochloride	63·986
C_2H_4	15·200
Dimethylaniline hydrochloride (calc.)	79·186
Anhydrous dimethylaniline hydrochloride found	79·257
Diff.	0·071

Aniline Hydrochloride.

It was only possible to examine this salt in solution; that used was an aqueous one of the composition $C_6H_7N,HCl + 9{\cdot}722OH_2$. The results for H_α are compared with the calculated, and are as follows.

Aniline hydrochloride (calc.)	63·986
„ „ found............	63·457
Reduction for solution	0·529

So that as in the case of dimethylaniline hydrochloride, solution in water evidently causes a fall in the molecular refraction. A small amount of this reduction may, however, be due to the saturation of the valencies of the nitrogen with the acid, as in the case of the rotation.

Influence of the Ortho-, Meta-, and Para-positions, also of the α- and β-positions of the Naphthalene Series.

Dr. Gladstone was kind enough to examine some of my specimens in connection with this subject, and the following are his results in reference to the xylenes, the methyl tolyl oxides, dimethylresorcinol, and veratrol.

	$\frac{\mu_A - 1}{d}p.$		$R_H - R_A$.
Paraxylene	59·96	− 0·02	4·92
Metaxylene	59·98	0·18	4·93
Orthoxylene............	59·80		4·85
Paratolyl methyl oxide ..	63·37	0·06	5·51
Metatolyl methyl oxide ..	63·31	0·06	5·48
Orthotolyl methyl oxide..	63·25		5·47
Veratrol	66·73	0·05	—
Dimethylresorcinol	66·68		5·98

From these results it is seen that para- and meta-xylene give nearly identical results, the meta- and para-tolyl methyl oxides differing rather more, whilst the ortho-compounds in all cases give the lowest number, especially in orthoxylene.

The same is seen to be the case with ortho- and para-toluidine.

		H_α.	H_β.	H_γ.
Paratoluidine......	49·6°	60·642	63·129	64·741
Orthotoluidine	49·0	60·585	63·028	64·632
		0·057	0·101	0·109

In the latter case, the numbers indicate a slight difference in dispersion also.

Landolt and Jahn's (*Zeit. physikal. Chem.*, 1892, **10**, 312) results for H_α show a similar but somewhat smaller difference between ortho- and meta-xylene (0·092), whilst Brühl's numbers give a rather larger difference, 0·380 (*J. pr. Chem.*, 1894, **50**, 149), so that ortho- evidently give lower results than para- and meta-compounds.

The α- and β-positions in the Naphthalene Series.

These positions may be regarded as similar to those of ortho-meta-, or para-, their influences are, however, more strongly marked thus.

	Line A.	H_α.	H_γ.
Ethyl β-naphthyl oxide	95·311	96·678	104·457
Ethyl α-naphthyl oxide	94·987	96·382	104·303
	0·324	0·296	0·154

In the naphthylamines, the differences are still larger.

	Line A.	H_α.	H_β.
β-Naphthylamine, 98°	85·054	86·670	92·192
α-Naphthylamine, 98°	84·018	85·469	90·928
	1·036	1·201	1·264

In this instance, the dispersion of the α- is evidently somewhat less than that of the β-compound, whilst in the oxides it appears to be slightly greater.

This subject of the influence of relative position in the benzene and naphthalene hydrocarbons, in connection with refraction and rotation, is of considerable interest. In all cases hitherto considered, these two properties have run parallel as to the kind of difference corresponding with variation in structure, but in the case of ortho-benzene and α-naphthalene compounds, the differences are of opposite kinds, being *plus* relatively to meta- and para- in the molecular rotation, but *minus* in the molecular refraction.

Ethereal Salts.

Ethylic Anisate and Ethylic Methylsalicylate.—These salts were examined because the former gives rotations which are much higher than would be expected, and it was therefore desirable to see whether this also applied to the molecular refraction. The numbers obtained were as follows.

	Line A.
Ethylic anisate	83·79
Ethylic methylsalicylate	83·04
	0·75

This comparison shows the same kind of difference as that in the rotations, because the ortho-compound should only be lower than the para- by a small amount, not more than from about 0·05 to 0·18. As the ortho-compound gives a normal rotation, it would be likely to have a normal refraction, and therefore is a suitable substance for comparison. This being so, the molecular refraction of ethylic anisate is evidently high, as in the case of the rotation.

Ethylic α- and β-Naphthoates.—These were also examined, because their rotations were peculiar; they gave

	H_α.	H_β.
Ethylic β-naphthoate......	105·580	110·776
Ethylic α-naphthoate......	104·206	109·280
	1·374	1·496

The largeness of these differences, which are otherwise of the ordinary character for variation in position, show that there is something peculiar in the behaviour of these substances. In the rotations, the α-compound was found to give a rather lower instead of a higher result than the β-compound, showing that its rotation is lower than might be expected; no doubt this is also the case with the refraction, thus making the above difference for position appear abnormally large.

SECTION V.—CONCLUSION.

From the foregoing results, it is seen that there is a great difference between the rotation of aromatic and fatty compounds, the effect of the nuclei contained in them greatly influencing their rotatory character.

It is found that in many cases the substances behave like double molecules, the part containing the fatty groups acting like a fatty compound when it is thoroughly screened off from the phenyl by carbonyl, whilst that containing the nucleus acts in a different manner. This is seen in the ethereal salts of the aromatic acids, where the alcohol radicles have practically the same influence on the rotation as when they displace hydrogen in the carboxyl of fatty acids, whereas the benzene nucleus they contain behaves in a distinct manner, as seen, for example, by the large numbers it gives when associated directly with a CH_2 group, or when its hydrogen is displaced by hydroxyl, &c. When the screening is not perfect, as when effected by CH_2, the fatty groups retain the general character of their rotation, and although augmented to some extent, they are not affected nearly as much as when in direct union with the nucleus.

The nucleus is also influenced by the groups and haloïds it is associated with, thus with NO_2 and fluorine its influence is very greatly reduced, and it is also reduced, but not to so great an extent, by CO and by chlorine; it is worth noticing that all these are strongly electronegative. On the other hand, it is increased by association with hydrocarbon groups, especially when unsaturated, and greatly so by the electropositive group, NH_2, and its methylated and phenylated derivatives. It is seen, therefore, that strongly electronegative elements and groups act differently and in an opposite manner to the electropositive group. With bromine, however, little or no change occurs, and with iodine a slight increase takes place.

It was originally supposed that the NO_2 and other groups, as well as some of the haloïds, owed their reducing influence on the rotations of the compounds in which they existed to their rotatory power being much less than that of the nucleus; this, however, seems to be disproved by the fact that the NH_2 group, which has also a relatively small rotation, acts strongly in an opposite direction. The remarkable rotations of nitro-compounds and of fluorobenzene may, however, be regarded from another point of view. It has been shown by Becquerel (*Ann. Chim. Phys.*, 1877, **12**, 51) that ferrous and ferric chlorides, which are paramagnetic salts, have the remarkable property, when in a magnetic field, of deviating the plane of polarisation of light in the opposite manner to diamagnetic bodies. For distinction, the rotation of the former is called *negative*, and the latter *positive*.

As the rotations of solutions of these salts include also that of the water, which has a *positive* rotation, they vary with the strength, because the rotations of the salt and water, being opposite, neutralise each other more or less, and the proportions of the two can be so arranged that they either have no rotation, or one of a positive or negative character. Iron compounds, however, do not always act in the same manner. Mond's iron carbonyl is both *diamagnetic*, and also has a *positive* rotation, like compounds of that class.

Oxygen is known to be paramagnetic in the free state, and Dewar has shown that it is strongly so when in the liquid condition.

It is, therefore, not impossible that the oxygen of the NO_2 in nitrobenzene may also be paramagnetic, and if so, this would account for the very low rotation of this compound, because the negative character of the oxygen it contains would neutralise the positive rotation of the other part of the substance, and thus reduce it. If this be so, the inference is that fluorine is also paramagnetic, as it acts in a similar manner.

Like iron, oxygen might not have this character in all compounds, and, in fact, its influence on the rotation of most substances shows that it cannot be so.

The very low rotation of sulphuric and phosphoric acids, although containing sulphur and phosphorus which have very large rotations, would become easily explainable if the oxygen they contain were paramagnetic. This would probably only be the case with that which is doubly linked, because in hydroxyl it appears to be always diamagnetic.

There still, however, remains the difficulty that in dinitrobenzene the second NO_2 group does not have a reducing influence on the rotation like the first, as, although the effect of the first displacement is to change the type of the substance, its behaviour then becomes normal. This subject, however, requires further examination because the behaviour of the NO_2 group in this particular substance is not consistent with the behaviour of the NH_2 group, which acts in the opposite direction. The second NH_2 group, although not having such a large influence as the first, is nevertheless very large. The further examination of a number of nitro- and dinitro-derivatives may throw light on this matter.

The variation in the influence of the nucleus on the rotations has been seen to be very considerable, even in hydrocarbons, and the way this influence varies when two or more nuclei become more and more nearly associated, and at last come into direct union, is very remarkable, for it is found that the more closely they are related in a compound the more does their influence on the rotation increase. In benzene, for example, the influence of C_6H_5 is 10·776; when two of these groups are associated but kept separate by CH_2, as in diphenylmethane, the average influence of both rises to 11·157, whilst if three are clustered around CH it becomes 11·493, but when the intervening group in diphenylmethane is removed, so that the two C_6H_5 groups are in direct union it rises to 12·398. From these results it is evident that these differences do not arise from the action of mass, seeing that the molecule of diphenyl differs but little in size from that of diphenylmethane, and is only about two-thirds the size of that of triphenylmethane.

That considerable changes in rotation occur which are not due to mass action, but to differences of relationship and structure, is seen in other cases; for example, diphenyl and acenaphthene are isomeric, yet the rotation of the latter is 3·3 higher than that of the former, and also the influence of the small group $N(CH_3)_2$ when introduced into naphthalene yields a compound with a rotation not very much less than twice that of the hydrocarbon itself.

Another interesting point which has been considered in reference to the benzene nucleus is its association with unsaturated carbon groups (see table, next page).

In the first case, where there is no benzene nucleus, it is practically the same as in the second, where there is one, but it is screened off by the CO group. In the third, where it is in direct union with the nucleus, it rises to 3·046, whilst in the fourth, where the unsaturated group has both ends in union with the nuclei it is no less than 8·166, or nearly 10 times as great as the first two differences, and more than twice that of the third. The following are examples.

	Mol. rot.	Diff. for H_2.
Hexane, $C_3H_7{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	6·646	0·827
Hexylene, $C_3H_7{\cdot}CH{:}CH{\cdot}CH_3$	7·473	
Propylic benzoate, $C_6H_5{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	14·873	0·849
Allylic benzoate, $C_6H_5{\cdot}CO{\cdot}O{\cdot}CH_2CH{:}CH_2$	15·722	
Propylbenzene, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	14·553	3·046
Allylbenzene, $C_6H_5{\cdot}CH{:}CH{\cdot}CH_3$	17·599	
Dibenzyl, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$	24·977	8·166
Stilbene, $C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5$	33·143	

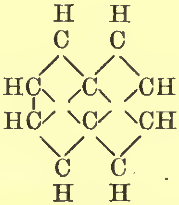
The direct association of the same kind of carbon groups as those of which the nucleus is composed is always very remarkable, as is seen when they are joined in a cyclic manner to the benzene nucleus, so as to form condensed nuclei such as naphthalene and phenanthrene, although probably the large rotation of these results partially from the existence in naphthalene of two, and in phenanthrene of four, carbon atoms unassociated with hydrogen, making them of a more unsaturated character than benzene.

From what has been seen, it is evident that no fixed value exists for the magnetic rotatory power of phenyl in hydrocarbons, and it is also evident that the rotations of other aromatic compounds do not give any regular value, either for this or for naphthyl; at the same time also, they do not give any consistent values for the groups which are directly united with the nuclei. Thus, the influence of NH_2 entering a paraffin raises its rotation by 0·971, but in benzene it raises it 4·792, and in naphthalene, for the α-position, 12·353. Now, it would be absurd to assume that this group has all these widely different values, or that the value of carbon and hydrogen in the nucleus has changed so as to share in this great increase; it is, at the same time, found that these great changes take place in cyclic compounds only, moreover, these changes, which affect the rotation in these molecular systems, are clearly not of a kind which is represented simply by the addition or subtraction of the usual value of NO_2, NH_2, $N(CH_3)_2$, &c.

The fact that in naphthalene both nuclei are apparently equally affected by the introduction of NO_2 or NH_2, although the displacement takes place in one only, shows this; and in these and many other instances one is led to believe that, in these compounds, there is a kind of inductive effect from one carbon group to another, the influence of some of the groups approximating to the ordinary values found in the fatty series being multiplied by the number of carbon atoms in the nuclei. Taking aniline as an example, the increase in rotation for the introduction of NH_2 into the nucleus, although not six times as great as the ordinary value of NH_2 in the fatty series, is yet very nearly five times that amount. In the naphthalene series, it is rather more than 10 times as great in β-naphthylamine, whilst in the corresponding α-compound it is 12 times as great. Much the same kind of thing is found in the dimethylated bases.

In the consideration of the rotations of pyridine, quinoline, and thiophen, an analogy is drawn between a chain of bar electromagnets and a circle of the same, the former being taken as representing an open chain compound, and the latter as representing benzene; the energy required to rupture these systems being supposed to represent the relative rotatory influence of these compounds, the latter being, of course, the greater. Now it is clear that if a second coil of wire were wound round one of the magnets of the circle and an electric current passed through it, the extra influence produced in this bar (which might be taken to represent the influence of the NH_2 group) would pass into all the others, and if the current were reversed its effect (which also might be taken as representing the influence of the NO_2 group) would weaken the whole system. This is given simply as an illustration of the above idea of induction from one carbon atom to another.

If this analogy be applied to naphthalene, as usually represented, consisting of two closed circles, of course no effect would be produced in the second circle, this, however, is not the case if it is represented by the concentric method, thus



Whatever may be the actual arrangement in the naphthalene molecule, the influence of the NO_2 and NH_2 groups being more than twice as large as in benzene, can only be understood on the assumption that both sides of the molecule are equally influenced.

Diphenylamine is an interesting example in reference to this subject, the two separate phenyl molecules being united by NH; the influence which this appears to have in this compound is not much less than twice that of NH (or NH_2 disp. H) in aniline, both molecules being equally influenced.

But whether these large rotations arise from an inductive influence in the nuclei of benzene and naphthalene, or from some other kind of action, it seems evident that these great changes in rotation must be chiefly due to physical influences, and that only a part of their effect can be attributed to the rotatory power of the atoms contained in the molecule. The high refractive power of these compounds apparently must also be due to the physical nature of the molecules, and not simply to their chemial composition.

It is doubtful, however, whether any one kind of physical condition would account for all that takes place in reference to the rotation of these nuclei compounds, as besides the largeness or smallness of the rotations there are other differences to be accounted for, such as position, &c.

The physical conditions due to the arrangement of the atoms in the molecules of saturated carbon compounds must evidently be more simple than those connected with the unsaturated and aromatic compounds; but they undoubtedly have an influence on the rotation, and in the paper published in 1884 (Trans., **45**, 563), when referring to the value given for the elements, it is remarked, "These values, as a matter of course, work very well when used for a series of compounds from which they have been deduced, but when applied to other homologous series give only approximate results." It was shown that although the CH_2 group in the paraffin and paraffin residue apparently has a constant influence, yet each series of compounds has an initial value of its own, dependent on the series group or special molecule, such as COOH, CO, COH, OH, &c., and for calculating the rotation of members of these different series, a set of series constant was prepared; the extreme fluctuations in the rotations of these saturated compounds, for these differences in structure amounting to 0·839. Now these variations cannot be due to changes in the rotatory powers of the elements, but must be caused by the physical conditions induced by molecular arrangements. These differences are found also in the consecutive displacements of hydrogen by chlorine and bromine in methane and in acetic acid, their influences not being constant.

With respect to the refractive power of saturated compounds, attention was lately drawn to the influence of chlorine and bromine in the ethylic salts of chloracetic and bromacetic acids (Trans., 1894, **65**, 418—419), showing that they also differ for consecutive displacements; the results being analogous to what takes place in the rotation.

In reference to the refraction of compounds containing carbon, hydrogen, and oxygen only, the fluctuations observed have often been regarded as due to experimental errors or impurity in the products, but most of them are no doubt real.

On comparing the average molecular refraction of substances of different classes, taking Brühl's values given in the tables at the end of volume 203 of the *Annalen*, it is found they vary considerably from the calculated numbers (in the case of the paraffins, Brühl's value for hexane and Thorpe's value for heptane are averaged), thus

	Diff. from calculated value.
Paraffins	+0·51
Alcohols	+0·29
Ethylene alcohol	+0·42
Glycerine	+0·59
Aldehydes	0·00
Fatty acids	−0·16
Ethylic salt	−0·22

In these averages, formic and acetic compounds have not been taken, as in the rotation it has been shown they do not really belong to the homologous series, and in the refraction it is found that the former evidently differs from other analogous compounds, although in acetic compounds the variation is small; moreover, considering that the numbers taken are single results, and not derived from averages, it would not be well to place any great importance on the variations they show as compared with other ethylic salts, and in the rotation the variations are but small.

	Diff. from calculated values.
Formic acid	+0·14
Ethylic formate	+0·23
Acetic acid	−0·25
Ethylic acetate	−0·38

From these two tables it is evident there is an analogy between the differences found for the molecular rotation and molecular refraction, because in both cases the paraffins and alcohols give higher numbers than the acids and ethylic salts, and also in the case of formic acid and its ethylic salt both give high results in reference to both properties.

The fluctuations in the refractions must, therefore, be real, and the values modified by molecular arrangement as in the rotation. As the numbers used in the calculations are only the average influences which the elements exert in different compounds, they must not be regarded as their physical constants.

What the relationship of these influences to the true values of the elements may be, it is impossible to determine with certainty, especially as there are but few elements suitable for examination in reference to their magnetic rotations, and even then the results refer, at any rate in cases such as the halogens, to their molecular, and not to their atomic, conditions, whilst others, such as sulphur and phosphorus, are often in the form of complex molecules.

In reference to the magnetic rotation, however, chlorine has been examined in solution in carbon tetrachloride, and this gave a rotation for a half mol. (2·172), rather higher than that found for the influence of chlorine in propylic chloride (1·733).

With respect to the refractive power of the elements, Dr. Gladstone has examined bromine, which also gives a rather higher value (16·23) than in carbon compounds (15·3), and sulphur which gives much the same result as the sulphur in carbon bisulphide, though a little higher. Carbon (diamond) (*Phil. Trans.*, 1870, 20) gave about the same value as in saturated carbon compounds (5·0).

This evidence, although scanty, points to the probability of the true values of the elements not being greatly different from the average influence they exert in the ordinary saturated carbon compounds, though perhaps rather higher; this is not improbable, because, as already mentioned, the molecular arrangement in these substances is comparatively simple.

It is here interesting to notice that in saturated ring compounds the structure, as might be expected, is also evidently simple, and like that of the ordinary chain compounds, because the influence of the CH_2 groups contained in them is apparently practically the same in both. But directly unsaturated groups occur in open chain compounds, and, consequently, greater complexity of the molecule exists, larger rotations and higher refractive powers manifest themselves, and these increase with each repetition of the unsaturated group; when, however, these unsaturated groups are united so as to form a cyclic compound, a much greater effect is produced, both on rotation and refraction, evidently due to the formation of a new molecular system.

Considering these products from the saturated to the unsaturated, and then to the cyclic condition, each step being accompanied with a *reduction* in composition of H_2, and at the same time a *rising* in rotation and refraction, and then a still larger increase on the formation of the nucleus, it becomes evident that it is the increase of molecular complexity that is the cause of the augmentation of these properties, and that it is not the composition of the substance which produces the effect. As previously stated, it would be difficult to believe that the true rotation or refractive power of an element could be a variable quantity.

Whilst it is seen that the values given for the rotations and refractive powers of the elements in the fatty series are not true values, it does not militate against their use, and no doubt in the future, as in the past, they will be found most useful numbers. This is also true of the different apparent values of phenyl in the aromatic series. The effect the other groups have on the rotation when in union with the nucleus or when separated from it by other groups, &c., all promise to be of value in the examination of new products, and are calculated to give information respecting their constitution; but it is necessary to bear in mind that none of these are true values of the elements, but are modified by molecular influences, which are, in the case of the nucloïd compounds, often of very much greater effect than that of the elements themselves.

Some of the subjects treated in this paper can only be considered as superficially dealt with; that of temperature differences, for example, where the small variations in the rotations for changes of temperature require to be measured with greater accuracy than it has been possible to do when examining the large number of substances referred to in connection with this subject; the object has been rather to obtain a general survey of the subject than to get finished results, notwithstanding much care was taken in the determinations given.

The subject of mixtures also deserves more attention.

Much more work remains to be done in reference to the rotations of aromatic compounds, such as a more thorough study of the phenols, mono- and poly-hydroxylic, and their methylic and other derivatives, and other series of substances, but it is thought that the foregoing results, although not so complete as could be wished, show some of the most striking points connected with this field of investigation.

SECTION VI.—EXPERIMENTAL RESULTS.

The products used in this investigation were, with a few exceptions, obtained from Kahlbaum or prepared in my own laboratory, and for the others I am indebted to the kindness of friends. With the exception of two or three specimens from the latter source, and those I prepared myself, all were carefully examined, and most of them purified by fractional distillation or other methods, before their rotations or other physical constants were determined.

A great deal of trouble was experienced in finding suitable subjects for this enquiry, for it was not simply a matter of measuring any substance which could be easily obtained, but it was necessary to select those which had isomers or nearly related compounds with which they might be compared, and were also of a nature suitable for examination. For example, taking the subject of position, ortho-compounds are frequently liquid at the ordinary temperature, or easily fusible, whilst the corresponding para-compounds being mostly solid, and often not fusible below 100°, are unsuitable for measurement when this is the case; this rendered it difficult to get a sufficient number of pairs of ortho- and para-compounds belonging to different classes of substances for the elucidation of their molecular rotation.

With fused substances, a difficulty occasionally arises, in consequence of their containing a very minute quantity of some crystalline impurity of a higher fusing point than that of the compound itself; this may sometimes be separated by filtering the melted product in a heated chamber, but this is not always successful. This minute amount of crystalline impurity, which often can scarcely be seen, so interferes with the polarised light that readings cannot be obtained.

The difficulty occasioned by the high fusing point of a substance has in a few cases been overcome by mixing it with an allied substance of lower melting point.

The presence of colour, except it be a pure yellow, is also a source of difficulty, and many substances, which are colourless when freshly prepared, after a short time become slightly brown or tinted with some other colour, and even if colourless when their examination is commenced, they become coloured if heated for any length of time, as in the determination of temperature difference. This is especially the case with the aromatic amines, so that it is often necessary to distil them in a current of hydrogen directly before use; in doing this I have found it best to distil rapidly into a cold receiver, so that the temperature of the distillate may be reduced as quickly as possible. The aromatic diamines are the most troublesome products in this respect, and I may instance the great difficulty which was experienced with orthophenylenediamine on this account; it had to be examined, dissolved in aniline, and at a temperature of about 74°. Starting with the two bases practically free from colour, by the time the solution was made, and the temperature adjusted in the measuring tube, the mixture had become so coloured that it was only on two occasions, out of numerous trials, that a moderately satisfactory measurement was obtained; the same was the case with dimethylparaphenylenediamine even at the ordinary temperature.

The measurement of substances in solution has been avoided as far as possible, as it is not only much more satisfactory to use the substance itself, but, as seen in the section on the rotation of mixtures, a source of error is introduced unless solvents with suitable specific rotations are employed.

In the particulars respecting the rotations (see Tables, p. 1236 *et seq.*) only the average of the results is given, and not all the details as in most of my previous papers; it will also be noticed that the rotations of most substances have been determined more than once, some of them six times. This is meant to imply that they have been examined on different occasions, not merely several times on the same day, so that any errors in one day's examination would not be likely to occur on the next, or might be of an opposite kind, and thus compensate each other.

It was expected that in the case of aromatic compounds, owing to their larger rotations, more exact results would be obtained than with the fatty compounds, but this has not been found to be the case. One cause of this is, that large angles cannot be determined with such an amount of accuracy as smaller ones, especially as any slight imperfection in the monochromatic light used causes the colour of the half discs of the polarising apparatus to become less uniform in shade as the angle increases; owing to this and to the molecular weights of the compounds being higher than those of most of the fatty series, the second place of decimals in the molecular rotations becomes more sensitive to small differences in the measurements; satisfactory results can be obtained, however, by taking the average of a large number of readings, made preferably on two or three different occasions, so that the errors of observation due to the varying condition of the eyes, or other changing circumstances, may be neutralised.

The number of readings made for each determination was usually 32, and sometimes 40, so that when it is stated that a substance was examined three times, it shows that the result is the average of three sets of readings, amounting in all to at least 96.

In the following pages, the results of the experimental work are given; first the relative densities, boiling point and method of preparation or source of the substance examined, followed by the determinations of the refractions. The specific and molecular rotations have been arranged separately in tabular form, it being considered better to group all the rotations together in this way, as it not only renders them more available for reference, but makes it much easier to compare the individual rotations of members of closely related groups of substances. Tables of boiling points follow, and finally an index in which the molecular rotation of each substance has been inserted.

Where solutions or mixtures have been employed in determining the rotation, the details of calculation have been given in the paragraph describing the substance.

FATTY COMPOUNDS.

1. *Heptane* (*from* Pinus sabiniana), C_7H_{16}.

Relative density:*

$d\,50° = 0·6665$.
$d\,55 = 0·6634$.
$d\,60 = 0·6604$.
$d\,65 = 0·6574$.
$d\,70° = 0·6546$.
$d\,75 = 0·6520$.
$d\,80 = 0·6493$.
$d\,85 = 0·6467$.
$d\,90° = 0·6441$.
$d\,95 = 0·6416$.

2. *Acetic acid*, $C_2H_4O_2$.

Relative density: $d\,21° = 1·0515$. $d\,86° = 1·0064$.

3. *Propionic acid*, $C_3H_6O_2$.

Relative density: $d\,20·3° = 0·9937$. $d\,91° = 0·9480$.

4. *Œnanthylic acid*, $C_7H_{14}O_2$.

Relative density: $d\,15° = 0·9224$. $d\,91·4° = 0·8893$.

5. *Ethylic Œnanthate*, $C_9H_{18}O_2$.

Relative density: $d\,15° = 0·8720$. $d\,92·1° = 0·8313$.

6. *Chloracetic acid*, $C_2H_3ClO_2$.

Relative density: $d\,64·5° = 1·3978$.

7. *Dichloracetic acid*, $C_2H_2Cl_2O_2$.

Relative density: $d\,13·5° = 1\ 5724$. $d\,90·7° = 1·5163$.

8. *Trichloracetic acid*, $C_2HCl_3O_2$.

Relative density: $d\,60·6° = 1·6298$.

9. *Dipropyl Ketone*, $C_7H_{11}O$.

Relative density: $d\,14·8° = 0·8210$. $d\,90° = 0·7804$.

10. *Ethylic Acetoacetate*, $C_6H_{10}O_3$.

Relative density: $d\,16·3° = 1·0307$. $d\,91° = 0·9839$.

11. *Dimethylacetylacetone*, $C_7H_{12}O_2$.

Relative density: $d\,19·3° = 0·9534$. $d\,92·3° = 0·9180$.

12. *Hydracetylacetone*, $C_5H_{10}O_2$.

Relative density: $d\,14·9° = 1·0001$. $d\,95·1 = 0·9507$.

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* The "relative density" is in all cases the density relative to water at the same temperature; d 50° for d 50°/50°.

13. *Ethylene Dichloride*, $C_2H_4Cl_2$.

Relative density: *d* 14·4° = 1·2606. *d* 62·5° = 1·2104.

14. *Octylic Chloride*,* $C_8H_{17}Cl$ (b. p. 183·6—184·6°, corr.).

Relative density: *d* 8·4° = 0·8838. *d* 90·6° = 0·8431.

15. *Propylic Bromide*, C_3H_7Br.

Relative density:

d 10·7° = 1·3699. *d* 15° = 1·3640. *d* 65·5° = 1·3012.

16. *Octylic Bromide*, $C_8H_{17}Br$ (b. p. 200·3—202·3°).

Relative density: *d* 13° = 1·1178. *d* 92·1° = 1·0732.

17. *Ethylic Iodide*, C_2H_5I.

Relative density:

d 11° = 1·9574. *d* 15° = 1·9492. *d* 64·3° = 1·8698.

18. *Octylic Iodide*, $C_8H_{17}I$.

Relative density:

d 16·5° = 1·3402. *d* 15° = 1·3416. *d* 81·9° = 1·2994.

19. *Methylene Diiodide*, CH_2I_2.

Purified by freezing and subsequent removal of oily products by continued rubbing on a porous plate.

Relative density: *d* 12·2° = 3·3394. *d* 15° = 3·3326.
d 55·4° = 3·2708. *d* 92° = 3·2445.

20. *Pyrotartaric Anhydride*, $C_5H_6O_3$.

Relative density: *d* 11·6° = 1·2418. *d* 50° = 1·2176.

21. *Ethylic Citraconate*, $C_9H_{14}O_4$.

Relative density: *d* 16° = 1·0471. *d* 76° = 1·0137.

22. *Citraconic Anhydride*, $C_5H_4O_3$.

Purified with phosphoric anhydride.

Relative density: *d* 17·4° = 1·2482. *d* 65·7° = 1·2174.

AROMATIC ETHEREAL SALTS.

23. *Methylic Benzoate*, $C_7H_5O_2{\cdot}CH_3$.

This was made from benzoic acid and methylic alcohol by the action of hydrogen chloride, most of its homologues referred to in this paper being prepared in an analogous manner. The specimen examined boiled at 198·6° (corr.).

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* This and the following four haloïd compounds were purified by a new method with sulphuric acid, which will be described in a future communication.

Relative density:
d 4° = 1·1035. *d* 10° = 1·0983. *d* 20° = 1·0904.
d 5 = 1·1026. *d* 15 = 1·0942. *d* 25 = 1·0869.

24. *Ethylic Benzoate*, $C_7H_5O_2{\cdot}C_2H_5$ (b. p. 211·7—211·9°, corr.).

Relative density:
d 4° = 1·0614. *d* 10° = 1·0562. *d* 20° = 1·0487.
d 5 = 1·0605. *d* 15 = 1·0523. *d* 25 = 1·0452.

25. *Propylic Benzoate*, $C_7H_5O_2(C_3H_7)$ (b. p. 230·6—230·9°, corr.).

Relative density:
d 4° = 1·0363. *d* 10° = 1·0314. *d* 20° = 1·0240.
d 5 = 1·0353. *d* 15 = 1·0276. *d* 25 = 1·0208.

26. *Isopropylic Benzoate*, $C_7H_5O_2{\cdot}CH(CH_3)_2$.

This was prepared by heating a mixture of benzoic chloride and isopropylic alcohol in the water bath, using an excess of the latter, as part of it is probably converted into isopropylic chloride by the hydrogen chloride evolved; the reaction does not go on at all rapidly at 100°. The product was then mixed with ether, washed twice with a solution of sodium carbonate, and dried over potassium carbonate. After the ether had been distilled off, the oil was fractionated a few times, when most of it boiled at 218—219° (corr.).

Relative density:
d 4° = 1·0263. *d* 10° = 1·0211. *d* 20° = 1·0135.
d 5 = 1·0254. *d* 15 = 1·0172. *d* 25 = 1·0103.

27. *Butylic Benzoate*, $C_7H_5O_2{\cdot}C_4H_9$ (nor.).

Normal butylic alcohol, obtained from Kahlbaum, was used; after being roughly fractionated, this was converted into the benzoate by means of hydrogen chloride, the benzoic acid being added by degrees, as etherification occurred, and until it no longer dissolved, as it is not very freely soluble in the alcohol. The product was then dissolved in ether, washed with dilute potash until decidedly alkaline, the ethereal solution dried, &c., when it boiled at 248·0—251°. After fractionating several times, the portion boiling at 248·5—249·5° was taken for examination.

Relative density:
d 4° = 1·0198. *d* 10° = 1·0147. *d* 20° = 1·0077.
d 5 = 1·0189. *d* 15 = 1·0111. *d* 25 = 1·0048.

28. *Isobutylic Benzoate*, $C_7H_5O_2{\cdot}CH_2{\cdot}CH(CH_3)_2$ (b. p. 241·5°).

Relative density:

d 4° = 1·0123. d 10° = 1·0073. d 20° = 1·0000.
d 5 = 1·0114. d 15 = 1·0035. d 25 = 0·9971.

29. *Octylic Benzoate*, $C_7H_5O_2{\cdot}C_8H_{17}$.

Prepared from octylic alcohol from *Heracleum spondylium* and benzoic chloride, the mixture being heated until the action, which was rather sluggish, was completed. It was then distilled under reduced pressure; the fraction passing over at 258·4—260·4° at 210 mm., which constituted most of the product, was taken for examination.

Relative density:

d 4° = 0·9758. d 10° = 0·9713. d 20° = 0·9647.
d 5 = 0·9751. d 15 = 0·9679. d 25 = 0·9621.

30. *Ethylic Phenylacetate*, $C_6H_5{\cdot}CH_2{\cdot}COOC_2H_5$.

This and the following ethereal salts were prepared from the pure acids, ethylic alcohol, and hydrogen chloride in the usual manner. It boiled at 227·1—227·6° (corr.).

Relative density:

d 4° = 1·0555. d 10° = 1·0502. d 20° = 1·0425.
d 5 = 1·0545. d 15 = 1·0462. d 25 = 1·0390.

31. *Phenylacetic or α-Toluic acid.*

To examine this acid it was dissolved in ethylic benzoate, in the proportion corresponding to 1 mol. of the acid to 2 of the ethereal salt.

Relative density: d 15° = 1·0805. d 25° = 1·0737.

The magnetic rotation was three times determined.

t.	Sp. rotation.	Mol. rotation.
16·2°	1·8026	40·439
	Less 2EtBz̄ at 16·2°	27·700
	Phenylacetic acid at 16·2 ..	12·739
	Corrected to 15·0°	12·735

32. *Ethylic Hydrocinnamate (Phenylpropionate)*, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOC_2H_5$ (b. p. 247—247·5°, corr.).

Relative density:

d 4° = 1·0302. d 35° = 1·0088. d 70° = 0·9932.
d 5 = 1·0292. d 40 = 1·0063. d 75 = 0·9916.
d 10 = 1·0251. d 45 = 1·0038. d 80 = 0·9902.
d 15 = 1·0212. d 50 = 1·0015. d 85 = 0·9890.
d 20 = 1·0177. d 55 = 0·9993. d 90 = 0·9879.
d 25 = 1·0144. d 60 = 0·9971. d 95 = 0·9869.
d 30 = 1·0116. d 65 = 0·9950. d 100 = 0·9861.

33. *Ethylic Cuminate* (*Ethylic Para-isopropylbenzoate*), $C_6H_4(C_3H_7)\cdot COOC_2H_5$ (b. p. 263·1—264·1°).

Relative density:

d 4° = 1·0071. d 10° = 1·0023. d 20° = 0·9953.
d 5 = 1·0062. d 15 = 0·9986. d 25 = 0·9922.

34. *Methylic Salicylate*, $OH\cdot C_6H_4\cdot COOCH_3$ (b. p. 222·2°, corr.).

Relative density:

d 4° = 1·1992. d 10° = 1·1933. d 20° = 1·1852.
d 5 = 1·1982. d 15 = 1·1890. d 25 = 1·1817.

35. *Ethylic Salicylate*, $OH\cdot C_6H_4\cdot COOC_2H_5$ (b. p. 233·5—234·0°, corr.).

Relative density:

d 4° = 1·1470. d 10° = 1·1413. d 20° = 1·1335.
d 5 = 1·1460. d 15 = 1·1372. d 25 = 1·1300.

36. *Ethylic Methylsalicylate*, $CH_3O\cdot C_6H_4\cdot COOC_2H_5$.

Prepared from oil of gaultheria, caustic potash, and methylic iodide dissolved in methylic alcohol, the mixture being heated at 100° in a sealed tube for a few hours; the product was washed with dilute potash to remove any unchanged oil of gaultheria. The methylic methylsalicylate thus obtained, which boiled at 253·4°, was then saponified, and the acid separated and purified. The methylsalicylic acid was then treated with alcohol and hydrogen chloride, and the ethereal salt washed with dilute alkali, dried, and distilled. Two preparations were made, and they both boiled at 261·5°.

Relative density:

d 4° = 1·1256. d 10° = 1·1201. d 20° = 1·1126.
d 5 = 1·1246. d 15 = 1·1162. d 25 = 1·1092.

37. *Ethylic Anisate*, $CH_3O\cdot C_6H_4\cdot COO\cdot C_2H_5$ (b. p. 269—270°).

This ethereal salt solidifies in a mixture of ice and salt to a beautiful crystalline mass which fuses at about +7°.

Relative density:

d 4° = 1·1185. d 10° = 1·1132. d 20° = 1·1059.
d 5 = 1·1175. d 15 = 1·1094. d 25 = 1·1028.

38. *Ethylic Metamethoxybenzoate*, $CH_3O\cdot C_6H_4\cdot COOC_2H_5$.

Methylic metamethoxybenzoate was first prepared by heating metahydroxybenzoic acid with methylic alcohol, caustic potash (2 mols.), and methylic iodide (2 mols.); the methylic salt thus obtained boiling at 252° (corr.). It was then saponified, and the acid separated and crystallised from alcohol; its melting point was 103·5°; Graebe gives 95°, Oppenheim and Pfaff 106—107°. The metamethoxybenzoic acid was then treated with ethylic alcohol and hydrochloric acid, and the resulting ethereal salt washed with dilute alkali. It boiled at 260—261° (corr.).

Relative density:
d 4° = 1·1147. d 10° = 1·1095. d 20° = 1·1019.
d 5 = 1·1138. d 15 = 1·1055. d 25 = 1·0987.

39. *Ethylic Orthotoluate and Paratoluate*, $CH_3{\cdot}C_6H_4{\cdot}COOC_2H_5$.

These were prepared by boiling the acids with absolute alcohol and about one-tenth of its volume of concentrated sulphuric acid for seven hours. The ethereal salts were washed with dilute sodium carbonate before distillation, the boiling points of these two being determined at the same time and with the same thermometer; the following difference was found.

		Diff.
Ethylic paratoluate..........	235·5°	8·5°
Ethylic orthotoluate	227·0	

Ethylic Orthotoluate (b. p. 227·0°, corr.).

Relative density:
d 4° = 1·0479. d 10° = 1·0428. d 20° = 1·0356.
d 5 = 1·0470. d 15 = 1·0390. d 25 = 1·0321.

Ethylic Paratoluate (b. p. 235·5°, corr.).

Relative density:
d 4° = 1·0393. d 10° = 1·0344. d 20° = 1·0271.
d 5 = 1·0384. d 15 = 1·0306. d 25 = 1·0240.

40. *Ethylic Phthalate*, $C_6H_4(COOC_2H_5)_2$ (b. p. 298—299°, corr.).

Relative density:
d 4° = 1·1358. d 35° = 1·1152. d 70° = 1·1019.
d 5 = 1·1348. d 40 = 1·1128. d 75 = 1·1008.
d 10 = 1·1306. d 45 = 1·1106. d 80 = 1·0997.
d 15 = 1·1268. d 50 = 1·1085. d 85 = 1·0988.
d 20 = 1·1234. d 55 = 1·1065. d 90 = 1 0980.
d 25 = 1·1205. d 60 = 1·1048.
d 30 = 1·1178. d 65 = 1·1032.

41. *Ethylic Meta- or Iso-phthalate*, $C_6H_4(COOC_2H_5)_2$.

Prepared by boiling the acid with alcohol and 10 per cent. of sulphuric acid for seven hours. It boiled at 302°. After separation and distillation, it was cooled in a mixture of ice and hydrochloric acid, when it solidified; it was then pressed between bibulous paper. It forms rather large, well-defined crystals, melting at 11·5°.

Relative density:

d 4° = 1·1389.
d 5 = 1·0379.
d 10° = 1·1331.
d 15 = 1·1289.
d 20° = 1·1254.
d 25 = 1·1225.

42. *Ethylic Terephthalate*, $C_6H_4\cdot(COOC_2H_5)_2$.

Terephthalic acid was converted into the crystalline chloride by acting on it with phosphorus pentachloride. It was then added to absolute alcohol in small portions at a time, boiling between each addition, as the reaction does not take place at once, but sets in after a little time, and then the mixture boils vigorously; on adding water, the ethereal salt separated as an oil, which solidified on cooling. It was placed on a porous plate to remove a little oily matter, and then crystallised from petroleum, from which it separated in long prisms. It boiled at 302° (corr.), and solidified at 43·2°.

The boiling point of the three isomeric ethereal salts, determined with the same thermometer and under a pressure of 760 mm., gave

		Diff.
Ethylic phthalate	298·5°	3·5°
,, isophthalate	302·0	0·0
,, terephthalate	302·0	

Relative density:

d 45° = 1·1098.
d 50 = 1·1076.
d 55 = 1·1056.
d 60 = 1·1036.
d 65° = 1·1017.
d 70 = 1·0999.
d 75 = 1·0982.
d 80 = 1·0965.
d 85° = 1·0952.
d 90 = 1·0942.
d 95 = 1·0935.
d 100 = 1·0929.

43. *Ethylic Benzoylacetate*, $C_6H_5\cdot CO\cdot CH_2\cdot COOC_2H_5$.

Relative density:

d 4° = 1·1311.
d 5 = 1·1302.
d 10 = 1·1259.
d 15 = 1·1219.
d 20 = 1·1185.
d 25 = 1·1154.
d 30 = 1·1126.
d 35° = 1·1099.
d 40 = 1·1073.
d 45 = 1·1050.
d 50 = 1·1029.
d 55 = 1·1008.
d 60 = 1·0990.
d 65 = 1·0973.
d 70° = 1·0957.
d 75 = 1·0943.
d 80 = 1·0930.
d 85 = 1·0919.
d 90 = 1·0910.
d 95 = 1·0903.
d 100 = 1·0896.

44. *α- and β-Ethylic Naphthoates*, $C_{10}H_7\cdot COOC_2H_5$.

These were obtained by etherifying the respective acids by means of absolute alcohol and about 2 per cent. of sulphuric acid, boiling the mixture for six or seven hours; the products were well washed with sodium carbonate before being rectified. These compounds do not differ very much in boiling points, thus

		Diff.
Boiling point of ethylic β-naphthoate (74 mm.)	224·0°	3·5°
,, ,, α-naphthoate ,, ,,	220·5	

The difference between the α- and β-naphthyl ethyl oxides is 2·4°. These determinations were made at the same time and with the same thermometer.

Ethylic α-Naphthoate (b. p. 220·5° under 74 mm. pressure).

Relative density :

d 4° = 1·1356.
d 5 = 1·1348.
d 10 = 1·1310.
d 15 = 1·1274.
d 20° = 1·1244.
d 25 = 1·1217.
d 30 = 1·1192.
d 35 = 1·1169.
d 40° = 1·1148.
d 45 = 1·1130.
d 50 = 1·1113.
d 55 = 1·1097.

Ethylic β-Naphthoate (b. p. 224° under 74 mm. pressure, solidifies at 32°).

Relative density :

d 15° = 1·1212.
d 20 = 1·1181.
d 25 = 1·1154.
d 30° = 1·1129.
d 35 = 1·1106.
d 40 = 1·1085.
d 45° = 1·1065.
d 50 = 1·1048.
d 55 = 1·1031.

45. *Phenylic Acetate*, $CH_3{\cdot}COOC_6H_5$.

Phenylic acetate, prepared from phenol and acetic chloride, was quickly washed with water and then with dilute sodium carbonate solution, dried, and fractionated, the portion boiling between 196° and 197·5° being collected separately; to this about 10 per cent. of acetic anhydride was added to act on any phenol that might be present, and the mixture boiled and fractionated. The portion boiling between 196·5 and 197° (corr.) was reserved for the determination.

Relative density :

d 4° = 1·0906.
d 5 = 1·0896.
d 10 = 1·0851.
d 15 = 1·0809.
d 20 = 1·0771.
d 25 = 1·0734.
d 30 = 1·0699.
d 35° = 1·0670.
d 40 = 1·0642.
d 45 = 1·0613.
d 50 = 1·0584.
d 55 = 1·0558.
d 60 = 1·0534.
d 65 = 1·0512.
d 70° = 1·0491.
d 75 = 1·0472.
d 80 = 1·0454.
d 85 = 1·0438.
d 90 = 1·0424.
d 95 = 1·0412.

46. *Phenylic Propionate*, $CH_3{\cdot}CH_2{\cdot}COOC_6H_5$.

For the preparation of this substance, see Trans., 1889, **55**, 546. The numbers given below are for the crystallised compound, of which the boiling point is 211° (corr.). Before it was obtained in this condition it was examined, and the boiling point found to be 211·5—212·5°. Its relative density at 15° was 1·0532, and it gave a molecular rotation of 13·976, which is considerably higher than that given by the crystallised product.

Relative density:

d 4° = 1·0643.
d 5 = 1·0632.
d 10° = 1·0584.
d 15 = 1·0542.
d 20° = 1·0504.
d 25 = 1·0467.

47. *Phenylic Butyrate*, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOC_6H_5$.

Prepared by the action of butyric chloride on phenol (see Trans., 1889, **55**, 547); b. p. 227—228° (corr.).

Relative density:

d 4° = 1·0363.
d 5 = 1·0352.
d 10° = 1·0307.
d 15 = 1·0267.
d 20° = 1·0230.
d 25 = 1·0197.

48. *Phenylic Œnanthate*, $C_7H_{13}O_2{\cdot}C_6H_5$.

Prepared by heating œnanthylic chloride (b. p. 175—176°, corr.) with about the calculated proportion of phenol until hydrogen chloride was no longer given off; the product was then dissolved in ether, and the ethereal solution, after being washed with dilute potash and dried over calcium chloride, was distilled. The œnanthate came over between 281·8° and 282·8° (corr.). Dilute aqueous potash does not act on it appreciably, even when heated, but it is decomposed by boiling with strong potash.

Relative density:

d 4° = 0·9905.
d 5 = 0·9896.
d 10 = 0·9856.
d 15 = 0·9819.
d 20 = 0·9785.
d 25 = 0·9756.
d 30 = 0·9729.
d 35° = 0·9704.
d 40 = 0·9681.
d 45 = 0·9659.
d 50 = 0·9638.
d 55 = 0·9619.
d 60 = 0·9600.
d 65 = 0·9584.
d 70° = 0·9567.
d 75 = 0·9552.
d 80 = 0·9541.
d 85 = 0·9530.
d 90 = 0·9520.
d 95 = 0·9510.

NITRO-DERIVATIVES OF AROMATIC HYDROCARBONS.

49. *Nitrobenzene*, $C_6H_5{\cdot}NO_2$.

Prepared from benzene from benzoic acid. Boiling point 210·8°.

Relative density:

d 4° = 1·2193.
d 5 = 1·2182.
d 10 = 1·2134.
d 15 = 1·2093.
d 20 = 1·2055.
d 25° = 1·2020.
d 30 = 1·1989.
d 35 = 1·1958.
d 40 = 1·1930.
d 45 = 1·1904.
d 50° = 1·1881.
d 55 = 1·1857.
d 60 = 1·1836.

50. *Metadinitrobenzene*, $C_6H_4(NO_2)_2$.

This was examined in solution in nitrobenzene, the proportions being $C_6H_4(NO_2)_2 + 3C_6H_5{\cdot}NO_2$.

Relative density of this solution:

d 15° = 1·2763. *d* 25° = 1·2691.

The magnetic rotations were three times determined.

t.	Sp. rotation.	Mol. rotation.
17·1°	1·6121	37·726
Less mol. rot. of 3 mols. $C_6H_5{\cdot}NO_2$ at 17°..		28·077
		9·649
Corrected to 15·0°		9·647

51. *Orthonitrotoluene*, $C_7H_7{\cdot}NO_2$ (b. p. 225·2—226·2°).

Relative density:

d 4° = 1·1742. *d* 10° = 1·1686. *d* 20° = 1·1605.
d 5 = 1·1732. *d* 15 = 1·1643. *d* 25 = 1·1572.

52. *Paranitrotoluene*, $C_7H_7{\cdot}NO_2$.

This was purified by crystallisation from alcohol.

Relative density:

d 55° = 1·1392. *d* 60° = 1·1375. *d* 65° = 1·1358.

53. *α-Nitronaphthalene*, $C_{10}H_7{\cdot}NO_2$.

This was examined in solution in nitrobenzene, the proportions being $C_{10}H_7{\cdot}NO_2 + 2C_6H_5{\cdot}NO_2$.

Relative density of this solution:

d 15° = 1·2302. *d* 25° = 1·2236.

The magnetic rotations gave:

t.	Sp. rotation.	Mol. rotation.
16·2°	2·0894	39·561
	Less mol. rot. 2 mols. $C_6H_5{\cdot}NO_2$..	18·720
		20·841
	Corrected to 15·0°	20·840

Hydroxy-derivatives of Aromatic Hydrocarbons.

54. *Phenol*, $C_6H_6O = C_6H_5{\cdot}OH$.

The specimens examined boiled at 182·5—182·7° (corr.).

Relative density:

d 35° = 1·0677. *d* 60° = 1·0580. *d* 85° = 1·0503.
d 40 = 1·0656. *d* 65 = 1·0562. *d* 90 = 1·0492.
d 45 = 1·0636. *d* 70 = 1·0546. *d* 95 = 1·0484.
d 50 = 1·0616. *d* 75 = 1·0530. *d* 100 = 1·0479.
d 55 = 1·0598. *d* 80 = 1·0516.

55. *Phenol and Water.*

This was in the proportion of equal molecules, *i.e.*, $C_6H_6O + H_2O$.

Relative density of this solution:

d 4° = 1·0723. *d* 10° = 1·0678. *d* 20° = 1·0613.
d 5 = 1·0715. *d* 15 = 1·0644. *d* 25 = 1·0587.

The magnetic rotations twice determined:

t.	Sp. rotation.	Mol. rotation.
15·5°	2·2394	13·095
	Less 1 mol. H_2O..	1·000
		12·095
	Corrected to 15·0°....	12·096

This is a little lower than the number deduced from fused phenol which at 15·0° is estimated at 12·167 or 0·072 diff.

56. *Orthocresol*, $C_7H_8O = CH_3{\cdot}C_6H_4{\cdot}OH$.

This boiled constantly at 191° (corr.). It can be kept in a liquid state at temperatures below its solidifying point for a long time, and if a little water be added it remains permanently liquid, like phenol.

Relative density:

d 15° = 1·0511. *d* 20° = 1·0477. *d* 25° = 1·0447.

57. *Paracresol*, $C_7H_8O = CH_3{\cdot}C_6H_4{\cdot}OH$.

When distilling this, it was found useful to add about 1 per cent. of sodium, otherwise it came over slightly yellow; it boiled at 202° (corr.). It remains liquid for some considerable time when cooled below its melting point. With a little water it remains liquid at ordinary temperature.

Relative density:

d 15° = 1·0390. *d* 20° = 1·0362. *d* 25° = 1·0336.

58. *Paracresol and Water.*

On adding water in molecular proportion to fused and cold paracresol ($C_7H_8O + H_2O$) they do not mix at first, but, after shaking occasionally during about half an hour, they form a transparent, homogeneous liquid; this does not deposit crystals on standing, although it becomes cloudy at times with changes of temperature. This often made the readings difficult and uncertain.

Relative density:
d 15° = 1·0321. d 20° = 1·0295. d 25° = 1·0269.

The magnetic rotations twice determined:

t.	Sp. rotation.	Mol. rotation.
23·4°	2·0184	13·749
	Less 1 mol. OH_2..	1·000
		12·749
	Corrected to 15·0°	12·768

59. *Metacresol*, $C_7H_8O = CH_3{\cdot}C_6H_4{\cdot}OH$.

This was prepared from thymol by heating it with phosphoric anhydride and fusing the product with alkali, the metacresol being afterwards separated by acidifying with hydrochloric acid and agitating with ether according to the method of Tiemann and Schotten (*Ber.*, 1878, **11**, 769); it boiled at 202° (corr.).

Relative density:
d 15° = 1·0390. d 20° = 1·0359. d 25° = 1·0333.

60. *Thymol*, $C_{10}H_{14}O = C_3H_7{\cdot}C_6H_3(CH_3){\cdot}OH$ [$CH_3 : OH : C_3H_7 = 1 : 3 : 4$].

It boils at 233·5° (corr.). Although thymol melts at 50° it may be cooled down to 0° without solidifying.

Relative density:
d 4° = 0·9872. d 50° = 0·9624. d 80° = 0·9538.
d 5 = 0·9863. d 55 = 0·9606. d 85 = 0·9526.
d 10 = 0·9825. d 60 = 0·9590. d 90 = 0·9514.
d 15 = 0·9790. d 65 = 0·9576. d 95 = 0·9504.
d 20 = 0·9757. d 70 = 0·9562.
d 25 = 0·9723. d 75 = 0·9549.

61. *Carvacrol*, $C_{10}H_{14}O = C_3H_7{\cdot}C_6H_3(CH_3){\cdot}OH$ [$CH_3 : OH : C_3H_7 = 1 : 2 : 4$].

This boiled constantly at 237·7° (corr.).

Relative density:
d 4° = 0·9884. d 10° = 0·9842. d 20° = 0·9782.
d 5 = 0·9877. d 15 = 0·9810. d 25 = 0·9756.

62. *Homopyrocatechol*, $C_7H_8O_2 = CH_3{\cdot}C_6H_3(OH)_2$ [$CH_3 : OH : OH = 1 : 3 : 4$].

This specimen was furnished me by W. H. Perkin, junr.

Relative density:

d 30° = 1·1686. d 40° = 1·1647. d 50° = 1·1607.
d 35 = 1·1667. d 45 = 1·1627.

63. *Resorcinol*, $C_6H_6O_2 = C_6H_4(OH)_2 = [1:3]$.

At first this was distilled under reduced pressure, but afterwards it was found better to distil it at the ordinary pressure in a current of carbonic anhydride, and cool the distillate as quickly as it came over; in this manner it was obtained nearly white. It had to be examined in aqueous solution, and, as this became coloured on keeping, especially when heated, it was prepared a short time only before required for measurement. Two solutions were examined, a supersaturated and a weaker one; the former was troublesome, because it had to be heated before use to get the solid into solution, and this made it dark yellow, rendering it difficult to measure its magnetic rotation accurately.

I. This solution contained 63·583 per cent. of resorcinol, and had the composition $C_6H_6O_2 + 3·5H_2O$.

Relative density of this solution:

d 15° = 1·1048 d 25° = 1·1024.

Magnetic rotation three times determined:

t.	Sp. rotation.	Mol. rotation.
16·6°	1·8621	15·599
	Less H_2O......	3·500
		12·099
	Corrected to 15·0°	12·090

II. This solution, which was not quite saturated, had the composition $C_6H_6O_2 + 14·066H_2O$, and contained 30·285 per cent. of resorcinol.

Relative density of this solution:

d 15° = 1·0662 d 20° = 1·0650.

Magnetic rotation three times determined:

t.	Sp. rotation.	Mol. rotation.
15·0°	1·3729	25·982
	Less H_2O......	14·066
		11·916

From these two solutions, the estimated rotation of the dry substance will be 12·285 at 15°.

64. *Pyrocatechol*, $C_6H_6O = C_6H_4(OH)_2$ [1 : 2].

This was examined in an aqueous solution of the composition $C_6H_6O_2 + 24·445 OH_2$, which contained 20 per cent. of pyrocatechin.

Relative density of this solution:

$d\ 15° = 1·0459.$ $d\ 25° = 1·0449.$

Magnetic rotation four times determined:

t.	Sp. rotation.	Mol. rotation.
15·0°	1·2691	37·073
	Less OH_2.....	24·445
		12·628

If this differs for solution in the same manner as resorcinol, the rotation of the dry compound will be 13·022 at 15°.

65. *Pyrogallol*, $C_6H_6O_3 = C_6H_3(OH)_3$ [1 : 2 : 3].

This boiled at 309° (corr.), and the distillate had a freezing point of 125·5°. Two specimens were examined, one distilled and the other the fused sublimed product. It had to be examined in aqueous solution; this had the composition $C_6H_5O_3 + 15·542$ mol. H_2O, and contained 31·053 per cent. of pyrogallol.

Relative density of this solution:

$d\ 15° = 1·1048.$ $d\ 25° = 1·1024.$

The magnetic rotation of both specimens gave very concordant results. The average is as follows:—

t.	Sp. rotation.	Mol. rotation.
16·0°	1·3824	28·211
	Less H_2O	15·542
		12·669

If this differs for solution as resorcinol, the rotation of the dry substance will be 13·029 at 16°.

66. *Creosol*, $C_8H_{10}O_2 = OH{\cdot}C_6H_3(CH_3){\cdot}OCH_3$ [$CH_3 : OCH_3 : OH =$ 1 : 3 : 4].

From W. H. Perkin, jun. Boiled at 130—131° under 50 mm. pressure.

Relative density:

$d\ 15° = 1·0956.$ $d\ 20° = 1·0920.$ $d\ 25° = 1·0886.$

67. *Isocreosol*, [$CH_3 : OH : OCH_3$: 1 : 3 : 4].

Prepared by W. H. Perkin, jun. Boiling point 222—223° (corr.) and 180—181° under 250 mm. pressure. Freezing point 37—39°. Came over as a pale yellow oil, which remains liquid for days at the ordinary temperatures.

Relative density:—
d 15° = 1·0973. d 25° = 1·0905. d 35° = 1·0845.
d 20 = 1·0938. d 30 = 1·0874. d 40 = 1·0819.

Mixed Oxides containing Aromatic Radicles.

Most of these were prepared by the action of the iodides of the alcohol radicles on an alcoholic solution of the phenol, and caustic alkali or sodium ethoxide, in molecular proportion, the mixture being heated in a closed vessel at 100° until the action was complete. After removing the excess of the alcohol by distillation, the residue was mixed with ether, the solution washed with water and caustic alkali, dried, and the ether removed by distillation; the product was then fractionally distilled several times.

When preparing phenyl octyl oxide, instead of employing alcohol as the solvent, an excess of phenol was used, and as this has a high boiling point the action readily took place on boiling the mixture; 3 mols. of phenol being used to one of caustic potash and one of octylic iodide. When adding the alkali to the phenol, a little water was also added to make the product liquid, the iodide was then added, and the mixture heated in a Wurtz flask. At first water and a little oil came over, the latter being returned to the flask; after boiling for about an hour, a little more caustic alkali was added and the boiling continued for another hour to completely remove the last traces of octylic iodide. The product was then dissolved in ether, washed with alkali until free from phenol, dried, the ether removed by distillation, and the product fractionated.

68. *Phenyl Methyl Oxide* (*Anisole*), $C_7H_8O = C_6H_5{\cdot}O{\cdot}CH_3$.

The boiling point of this specimen was 153·7—154·1° (corr.).

Relative density:
d 4° = 1·0077. d 10° = 1·0029. d 20° = 0·9951.
d 5 = 1·0070. d 15 = 0·9988. d 25 = 0·9915.

69. *Phenyl Ethyl Oxide* (*Phenetole*), $C_8H_{10}O = C_6H_5{\cdot}O{\cdot}C_2H_5$.

The boiling point was 170·2—170·5° (corr.).

Relative density:
d 4° = 0·9792. d 10° = 0·9742. d 20° = 0·9663.
d 5 = 0·9784. d 15 = 0·9702. d 25 = 0·9629.

70. *Phenyl Propyl Oxide*, $C_9H_{12}O = C_6H_5{\cdot}O{\cdot}C_3H_7$.

The specimen examined boiled at 189·1—189·6° (corr.).

Relative density:
d 4° = 0·9617. d 10° = 0·9568. d 20° = 0·9494.
d 5 = 0·9609. d 15 = 0·9530. d 25 = 0·9459.

71. *Phenyl Isopropyl Oxide*, $C_9H_{12}O = C_6H_5{\cdot}O{\cdot}CH(CH_3)_2$.

The boiling point was 177·0—177·5° (corr.).

Relative density:
d 4° = 0·9558. *d* 10° = 0·9505. *d* 20° = 0·9426.
d 5 = 0·9548. *d* 15 = 0·9464. *d* 25 = 0·9389.

72. *Phenyl Isobutyl Oxide*, $C_{10}H_{14}O = C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(CH_3)_2$.

It boiled at 199·4—200·4° (corr.).

Relative density: *d* 10° = 0·9366. *d* 20° = 0·9295.
d 15 = 0·9331. *d* 25 = 0·9262.

73. *Phenyl Octyl Oxide*, $C_{14}H_{22}O = C_6H_5{\cdot}O{\cdot}C_8H_{17}$.

This is a colourless oil which solidifies to a crystalline mass when cooled with ice and salt, and melts at 8°. The specimen examined boiled at 284·7—285·7° (corr.).

Relative density:
d 4° = 0·9217. *d* 10° = 0·9174. *d* 20° = 0·9108.
d 5 = 0·9209. *d* 15 = 0·9139. *d* 25 = 0·9081.

74. *Orthotolyl Methyl Oxide*, $C_8H_{10}O = CH_3{\cdot}C_6H_4{\cdot}O{\cdot}CH_3$.

This is a colourless oil boiling at 170·1—172·1° (corr.).

Relative density: *d* 10° = 0·9890. *d* 20° = 0·9816.
d 15 = 0·9851. *d* 25 = 0·9781.

75. *Paratolyl Methyl Oxide*, $C_8H_{10}O = CH_3{\cdot}C_6H_4{\cdot}O{\cdot}CH_3$.

It boiled at 176·5°.

Relative density:
d 4° = 0·9844. *d* 10° = 0·9794. *d* 20° = 0·9722.
d 5 = 0·9835. *d* 15 = 0·9757. *d* 25 = 0·9689.

76. *Metatolyl Methyl Oxide*, $C_8H_{10}O = CH_3{\cdot}C_6H_4{\cdot}O{\cdot}CH_3$.

The boiling point was 176·5—177·0°.

Relative density:
d 4° = 0·9852. *d* 10° = 0·9804. *d* 20° = 0·9731.
d 5 = 0·9844. *d* 15 = 0·9766. *d* 25 = 0·9697.

77. *Dimethylresorcinol*, $C_8H_{10}O_2 = C_6H_4(OCH_3)_2$ [1 : 3].

This substance after being fractionated several times boiled at 216·5—217·7° (corr.).

Relative density:
d 4° = 1·0705. *d* 10° = 1·0654. *d* 20° = 1·0583.
d 5 = 1·0696. *d* 15 = 1·0617. *d* 25 = 1·0552.

78. *Guaiacol*, $C_7H_8O_2 = OH{\cdot}C_6H_4{\cdot}OCH_3$ [1 : 2].

This beautifully crystalline product was obtained from Kahlbaum. It boiled constantly at 205·0° (corr.), and the freezing point was 28·3°. The fused product remains liquid at the ordinary temperature for months.

Relative density:

d 4° = 1·1492. *d* 15° = 1·1395. *d* 30° = 1·1288.
d 5 = 1·1481. *d* 20 = 1·1356. *d* 35 = 1·1259.
d 10 = 1·1436. *d* 25 = 1·1322. *d* 40 = 1·1230.

79. *Orthodimethoxybenzene* (*Veratrole*), $C_8H_{10}O_2 = C_6H_4(OCH_3)_2$.

I. This was prepared by acting on the potassium compound of guaiacol with methylic iodide. To prepare the potassium compound of guaiacol, Hlasiwitz's process was employed (*Ann.*, 1858, 106·365), the guaiacol used being obtained by repeated fractionation of the commercial oily product. It nearly all came over at 207·0—207·5° (corr.), and this fraction was taken for examination.

Relative density:

d 4° = 1·0962. *d* 10° = 1·0908. *d* 20° = 1·0833.
d 5 = 1·0952. *d* 15 = 1·0869. *d* 25 = 1·0799.

II. Since the above specimen was examined, Kahlbaum has commenced preparing this substance. A specimen obtained from him, and boiling at 207·1° (corr.), was examined.

Relative density:

d 4° = 1·1004. *d* 10° = 1·0953. *d* 20° = 1·0877.
d 5 = 1·0996. *d* 15 = 1·0914. *d* 25 = 1·0842.

80. *Dimethylquinol*, $C_8H_{10}O_2 = C_6H_4(OCH_3)_2$ [1 : 4].

This boiled constantly at 212·6° (corr.), and distilled over as colourless as water.

Relative density:

d 55° = 1·0526. *d* 75° = 1·0447. *d* 95° = 1·0394.
d 60 = 1·0504. *d* 80 = 1·0430. *d* 100 = 1·0386.
d 65 = 1·0484. *d* 85 = 1·0416.
d 70 = 1·0465. *d* 90 = 1·0403.

81. *Dimethylhomopyrocatechol*, $C_9H_{12}O_2 = CH_3{\cdot}C_6H_3(OCH_3)_2$ [$CH_3 : OCH_3 : OCH_3 = 1 : 3 : 4$].

The first specimen examined was prepared from creosol obtained by repeatedly fractionating beachwood tar. This, after being mixed with rather more than its own bulk of ether, was converted into the potassium derivative by means of a concentrated alcoholic solution of potash, and the crystalline product purified by strongly pressing it between calico, thoroughly mixing it with more ether, and again pressing it; it was then methylated by heating with methylic alcohol and methylic iodide in a sealed tube at 100°. The product prepared in this manner, after being washed with alkali and dried, was fractionated several times, and at length a specimen was obtained boiling at 219—222° (corr.).

Specimen II was prepared lately from creosol obtained from Kahlbaum; this was fractionated several times, and the fraction boiling at 213—219° was methylated. (It was not converted into the potassium salt like the above for further purification.) The product, after repeated fractionation, boiled at 219—221° (corr.).

Specimen I (b. p. 219—222°, corr.).

Relative density:

d 4° = 1·0687. d 10° = 1·0634. d 20° = 1·0560.
d 5 = 1·0678. d 15 = 1·0595. d 25 = 1·0525.

Specimen II (b. p. 219—221°, corr.).

Relative density:

d 4° = 1·0653. d 10° = 1·0601. d 20° = 1·0526.
d 5 = 1·0643. d 15 = 1·0562. d 25 = 1·0491.

82. *Trimethylpyrogallol*, $C_6H_6O_3 = C_6H_3(OCH_3)_3$ [1 : 2 : 3].

This boiled at 241° (corr.).

Relative density:

d 45° = 1·1118. d 65° = 1·1026. d 85° = 1·0954.
d 50 = 1·1094. d 70 = 1·1006. d 90 = 1·0942.
d 55 = 1·1071. d 75 = 1·0987. d 95 = 1·0932.
d 60 = 1·1049. d 80 = 1·0970. d 100 = 1·0925.

83. *α-Naphthyl Ethyl Oxide*, $C_{12}H_{12}O = C_{10}H_7{\cdot}O{\cdot}C_2H_5$.

Prepared by heating an alcoholic solution of α-naphthol with potash and ethylic iodide in a sealed tube at 100° for about three hours. The ethereal solution of the product was washed with alkali, dried, and distilled. After the ether had passed over it distilled at 279·6—281°, leaving a little residue; the distillate was yellow, but on rectifying a few times from small quantities of sodium, it was obtained colourless, and boiled at 279·6—280°.

Relative density:

d 4° = 1·0711. d 20° = 1·0605. d 40° = 1·0513.
d 5 = 1·0703. d 25 = 1·0579. d 45 = 1·0495.
d 10 = 1·0668. d 30 = 1·0555. d 50 = 1·0479.
d 15 = 1·0635. d 35 = 1·0533. d 55 = 1·0465.

84. *β-Naphthyl Ethyl Oxide*, $C_{12}H_{12}O = C_{10}H_7{\cdot}O{\cdot}C_2H_5$.

This was prepared in the same manner as the α-compound, substituting the β-naphthol for the α-naphthol; the contents of the sealed tube were mixed with water, and the β-naphthyl ethyl oxide, which is solid, was collected, washed with water, and then melted and shaken with dilute potash. After solidification and drying, it was distilled, but became slightly violet on keeping; this coloration, however, disappeared when it was exposed to sunlight. It was afterwards pressed between calico to remove a little oily matter, and crystallised from alcohol, when it was obtained quite white. Its boiling point was 282·0° (corr.), or 2·4° higher than that of the α-compound, the two being distilled the one directly after the other, using the same thermometer.

Relative density:

d 20° = 1·0640. *d* 35° = 1·0568. *d* 50° = 1·0510.
d 25 = 1·0615. *d* 40 = 1·0547. *d* 55 = 1·0493.
d 30 = 1·0590. *d* 45 = 1·0528.

Two methods of estimating the rotation of β-naphthyl ethyl oxide at 15° may be employed.

Mol. rotation.
I. α-Naphthol........... 43·4° = 31·777
β-Naphthol........... 41·9 = 30·247
1·530

difference between α- and β-compounds at about the same temperature. Apply this to the rotation of the α-compound at 15° to get rotation of β- at 15°.

α-Naphthol at 15° = 32·245
minus 1·530
β-Naphthol at 15° = 30·775

II. Estimated from temperature change of the α-compound—

β-Naphthol at 41·9° .... = 30·247
Temp. change of α-naphthol for 26·9° = 0·451
β-naphthol at 15° .... = 30·698

Both methods give fairly similar results.

85. *Benzyl Methyl Oxide*, $C_8H_{10}O = C_6H_5{\cdot}CH_2{\cdot}O{\cdot}CH_3$ (b. p. 170·5°).

Relative density:

d 4° = 0·9805. *d* 10° = 0·9751. *d* 20° = 0·9675.
d 5 = 0·9795. *d* 15 = 0·9711. *d* 25 = 0·9643.

AROMATIC HYDROCARBONS.

86. *Benzene*, C_6H_6.

The benzene used in the following measurements was prepared by distilling calcium benzoate with lime; the product was then rectified on a water bath, treated twice with concentrated sulphuric acid, washed, and dried with potassium carbonate; finally it was distilled from phosphoric anhydride. It boiled constantly at 80·3°. When collected in four fractions, and the density of the first and last being determined, the results were identical, showing it to be perfectly homogeneous.

Relative density:

d 5° = 0·8949.
d 10 = 0·8900.
d 15 = 0·8853.
d 20 = 0·8809.
d 25 = 0·8767.
d 30° = 0·8727.
d 35 = 0·8687.
d 40 = 0·8649.
d 45 = 0·8612.
d 50 = 0·8576.
d 55° = 0·8542.
d 60 = 0·8507.
d 65 = 0·8473.
d 70 = 0·8440.

87. *Toluene*, $C_6H_5\cdot CH_3$.

Coal-tar toluene, boiling at 110—110·5°, was sulphonated, the sulphonic acids converted into the calcium salts, and the para-salt separated by crystallisation; the potassium salt prepared from this was purified by two or three recrystallisations, powdered, mixed with slightly diluted sulphuric acid, and boiled in a retort, steam being passed through the product at the same time. Hydrolysis soon set in, and toluene distilled over. When dried and distilled from phosphoric anhydride, it boiled constantly at 110·6° corr., and the densities of the first and last of the five fractions obtained on distillation were identical. The relative density of the coal-tar toluene used for the preparation of this pure product was *d* 15° = 0·8695, which is 0·0025 lower than that of the latter, owing, no doubt, to the removal of hydrocarbons of the fatty series. Kahlbaum (*Siedetemp. u. Druck*, 95) gives the boiling point of toluene as 111° at 760 mm., and Warren (*Zeits. f. Chem.*, 1865, 666) as 110·3°.

Relative density:

d 4° = 0·8812.
d 5 = 0·8803.
d 10 = 0·8762.
d 15 = 0·8723.
d 20 = 0·8684.
d 25 = 0·8649.
d 30 = 0·8614.
d 35° = 0·8580.
d 40 = 0·8548.
d 45 = 0·8518.
d 50 = 0·8490.
d 55 = 0·8463.
d 60 = 0·8436.
d 65 = 0·8408.
d 70° = 0·8381.
d 75 = 0·8355.
d 80 = 0·8330.
d 85 = 0·8306.
d 90 = 0·8283.
d 95 = 0·8260.
d 100 = 0·8237.

88. *Ethylbenzene*, $C_6H_5{\cdot}C_2H_5$.

I. A quantity of this hydrocarbon from Kahlbaum was repeatedly fractionated. The specimen selected for examination had a boiling point of 135·5—135·7° (corr.).

Relative density:

d 4° = 0·8829. *d* 10° = 0·8780. *d* 20° = 0·8705.
d 5 = 0·8821. *d* 15 = 0·8741. *d* 25 = 0·8671.

II. A second specimen was also examined, prepared by the hydrolysis of the pure sulphonic acid of this hydrocarbon, and for which I am indebted to Dr. Moody. Boiling point, 135·5°.

Relative density:

d 4° = 0·8809. *d* 10° = 0·8759. *d* 20° = 0·8685.
d 5 = 0·8800. *d* 15 = 0·8720. *d* 25 = 0·8650.

89. *Propylbenzene*, $C_6H_5{\cdot}C_3H_7$.

The process employed for the preparation of this hydrocarbon was that of Fittig, Schaffer, and König (*Annalen*, 1869, **149**, 324), namely, the action of sodium on a mixture of bromobenzene and propylic bromide. To remove the last traces of bromine from the hydrocarbon thus obtained, it was repeatedly boiled with sodium until the metal remained bright. It was then fractioned a few times, and the portion boiling between 159° and 159·5° selected for examination. This fraction constituted the chief part of the product.

Relative density:

d 4° = 0·8753. *d* 10° = 0·8705. *d* 20° = 0·8634.
d 5 = 0·8745. *d* 15 = 0·8668. *d* 25 = 0·8603.

90. *Isobutylbenzene*, $C_6H_5{\cdot}C_4H_9$.

Purified by fractional distillation, it boiled at 169—169·5°.

Relative density:

d 4° = 0·8796. *d* 10° = 0·8748. *d* 20° = 0·8680.
d 5 = 0·8790. *d* 15 = 0·8714. *d* 25 = 0·8650.

91. *Orthoxylene*, $C_6H_4(CH_3)_2$ [1 : 2].

Obtained from Langfeld and Reuter. After distillation from phosphoric anhydride, it boiled at 142·1—143·1° (corr.).

Relative density:

d 4° = 0·8903. *d* 10° = 0·8854. *d* 20° = 0·8783.
d 5 = 0·8895. *d* 15 = 0·8818. *d* 25 = 0·8752.

92. *Metaxylene*, $C_6H_4(CH_3)_2$ [1 : 3].

I. From Langfeld and Reuter. After distillation from phosphoric anhydride, it boiled at 139·3° (corr.). Three fractions were collected, and the densities of the first and last taken; they only differed by 0·0007, so that the product was practically homogeneous.

Relative density:
d 4° = 0·8779. *d* 10° = 0·8728. *d* 20° = 0·8656.
d 5 = 0·8770. *d* 15 = 0·8691. *d* 25 = 0·8625.

II. This second specimen was prepared by the hydrolysis of pure sodium metaxylenesulphonate [1 : 3 : 4], and for its use I am indebted to Dr. Moody. When distilled from phosphoric anhydride, it boiled at 139·3°; it was collected in three fractions, the difference in the densities of the first and last being only 0·00008.

Relative density:
d 4° = 0·8779. *d* 10° = 0·8728. *d* 20° = 0·8656.
d 5 = 0·8770. *d* 15 = 0·8691. *d* 25 = 0·8625.

93. *Paraxylene*, $C_6H_4(CH_3)_2$ [1 : 4].

This was purified by strongly pressing the crystallised hydrocarbon between calico for some time. When distilled from phosphoric anhydride, it boiled constantly at 137·5° (corr.).

Relative density:
d 15° = 0·8661. *d* 20° = 0·8626. *d* 25° = 0·8593.

94. *Mesitylene*, $C_6H_3(CH_3)_3$ [1 : 3 : 5].

This was purified by repeated treatment with sulphuric acid until the acid was only coloured yellow; it was then steam-distilled; sulphuric acid was then scarcely coloured when shaken with it. After drying, it was distilled from phosphoric anhydride, and the fraction boiling at 163·6—164·6° (corr.) taken for examination.

Relative density:
d 4° = 0·8768. *d* 35° = 0·8565. *d* 70° = 0·8410.
d 5 = 0·8760. *d* 40 = 0·8540. *d* 75 = 0·8392.
d 10 = 0·8722. *d* 45 = 0·8516. *d* 80 = 0·8374.
d 15 = 0·8685. *d* 50 = 0·8493. *d* 85 = 0·8358.
d 20 = 0·8652. *d* 55 = 0·8471. *d* 90 = 0·8342.
d 25 = 0·8620. *d* 60 = 0·8449. *d* 95 = 0·8328.
d 30 = 0·8592. *d* 65 = 0·8429.

95. *Pseudocumene*, $C_6H_3(CH_3)_3$ [1 : 3 : 4].

Obtained from Langfeld and Reuter. It was purified in the same manner as the mesitylene, and then fractionated several times from phosphoric anhydride, by which means a small quantity of impurities of low and high boiling points were separated. The portion boiling at 168·0—168·5° (corr.) was then fractionated into three equal parts, and their densities taken. The first two had practically the same densities, and the third was only 0·0007 higher than the others. The first two were taken for examination.

Relative density:

d 4° = 0·8888.
d 5 = 0·8880.
d 10 = 0·8844.
d 15 = 0·8810.
d 20 = 0·8778.
d 25 = 0·8747.
d 30 = 0·8719.
d 35° = 0·8692.
d 40 = 0·8667.
d 45 = 0·8643.
d 50 = 0·8620.
d 55 = 0·8598.
d 60 = 0·8578.
d 65 = 0·8560.
d 70° = 0·8544.
d 75 = 0·8526.
d 80 = 0·8510.
d 85 = 0·8494.
d 90 = 0·8478.
d 95 = 0·8465.

96. *Cumene.* *Isopropylbenzene*, $C_6H_5{\cdot}CH(CH_3)_2$.

For the preparation of this hydrocarbon, barium cuminate, intimately mixed with four times its weight of baryta, was distilled in a long combustion tube in a slow current of hydrogen, the heating being commenced at the back end of the tube, and gradually carried forward. The oil obtained in this way was roughly fractionated to separate it from products of high boiling point, and then treated several times with small quantities of sulphuric acid, and afterwards with strong chromic mixture. The oil thus purified, after being washed and dried, was distilled; at first a small quantity of liquid of low boiling point came over, but the temperature then rose quickly; the distillate, after being fractionated several times, mostly passed over at 152·2—153·7° (corr.). This fraction was used for examination.

Relative density:

d 4° = 0·8753.
d 5 = 0·8745.
d 10° = 0·8705.
d 15 = 0·8668.
d 20° = 0·8634.
d 25 = 0·8603.

97. *Cymene*, $CH_3{\cdot}C_6H_4{\cdot}C_3H_7$ [1 : 4].

The hydrocarbon obtained from oil of cumin and boiling at 177° was first examined; it gave a relative density of *d* 15° = 0·8603 and a molecular rotation of 15·001, but as the purity of this product was doubted, it was converted into a sulphonic acid, and after the barium salt had been purified by repeated crystallisation, it was hydrolysed by heating with very strong hydrochloric acid for some hours in sealed tubes at 190—195°. The cymene thus obtained was steam-distilled, and afterwards fractionated, when it nearly all came over between 177·0° and 177·5° (corr.), and gave a molecular rotation of 15·255.

Relative density:

d 4° = 0·8701.
d 5 = 0·8693.
d 10° = 0·8654.
d 15 = 0·8619.
d 20° = 0·8586.
d 25 = 0·8558.

It is seen from the foregoing that although the cymene from oil of cumin has the same boiling point as that obtained from the sulphonic acid, yet the two differ in density and magnetic rotation, the product from the sulphonic acid being no doubt much the purer of the two.

98. *Naphthalene*, $C_{10}H_8$.

Relative density: d 85° = 1·0070. d 95° = 1·0056.

99. *Solution in Toluene.*

The strongest solution of this hydrocarbon in toluene that could be conveniently used was in the proportion of 1 mol. to 4 mols., that is, $C_{10}H_8 + 4C_7H_8$ = 25·806 per cent. solution.

Relative density: d 15° = 0·9088. d 25° = 0·9017.

The magnetic rotation three times determined

t.	Sp. rotation.	Mol. rotation.
15·8°	2·4310	73·757
	Less rot. 4 mols. $C_{10}H_8$	48·628
		25·129
	Corrected to 15·0°....	25·125

100. *Diphenylmethane*, $C_{13}H_{12} = CH_2(C_6H_5)_2$ (b. p. 264·7°, corr.).

Relative density:

d 25° = 1·0056.
d 30 = 1·0032.
d 35 = 1·0009.
d 40 = 0·9987.
d 45 = 0·9967.
d 50° = 0·9950.
d 55 = 0·9934.
d 60 = 0·9919.
d 65 = 0·9906.
d 70 = 0·9893.
d 75° = 0·9881.
d 80 = 0·9870.
d 85 = 0·9860.
d 90 = 0·9851.
d 95 = 0·9844.

101. *Dibenzyl*, $C_{14}H_{14} = C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$.

Boiled at 281—282° (corr.). Its freezing point was 51·4°.

Relative density:

d 50° = 0·9782.
d 55 = 0·9766.
d 60° = 0·9752.
d 65 = 0·9738.
d 70° = 0·9725.
d 75 = 0·9713.

Magnetic rotation, once determined

t.	Sp. rotation.	Mol. rotation.
57·6°	2·3853	24·713
Temp. diff. diphenylmethane (0·00621) 42·6°		0·264
Corrected to 15·0°......................		24·977

102. *Triphenylmethane*, $C_{19}H_{16} = CH(C_6H_5)_3$.

Relative density: d 95° = 1·0568. d 100° = 1·0570.

The magnetic rotations, twice determined, gave

t.	Sp. rotation.	Mol. rotation.
93·0°	2·7700	35·527
Temp. diff. of diphenylmethane (0·00621) 78°		0·484
Corrected to 15·0°		36·011

103. *Phenanthrene*, $C_{14}H_{10}$.

Solution in Toluene.

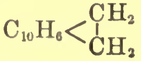
This hydrocarbon was purified by adding it to a small quantity of carbon bisulphide, filtering the solution, and heating it until free from the solvent, it was then crystallised from alcohol.

The solution examined had the composition $C_{14}H_{10} + 6C_7H_8$, and therefore contained 24·383 per cent. of phenanthrene.

Relative density: *d* 15° = 0·9196. *d* 25° = 0·9129.

The magnetic rotations, three times determined, gave

t.	Sp. rotation.	Mol. rotation.
16·0°	2·4903	109·897
	Less rot. of 6 mols. C_7H_8 =	72·942
	Corrected to 15·0°........	36·955



104. *Acenapthene*, $C_{12}H_{10} = C_{10}H_6<\begin{matrix}CH_2\\ | \\CH_2\end{matrix}$ (b. p. 229·5°, corr.).

Relative density: *d* 95° = 1·0687. *d* 100° = 1·0685.

The magnetic rotations, once determined, gave

t.	Sp. rotation.	Mol. rotation.
99·0°	3·5284	28·252
Temp. diff. of naphthalene (0·00457) 84°		0·384
Corrected to 15·0°		28·636

105. *Diphenyl*, $C_{12}H_{10} = C_6H_5{\cdot}C_6H_5$.

Relative density: *d* 95° = 1·0135. *d* 100° = 1·0126.

The magnetic rotation, twice determined, gave

t.	Sp. rotation.	Mol. rotation.
93·8°	2·9402	24·815
Temp. diff. of diphenylmethane (0·00621) 78·8°		0·489
Corrected to 15·0°		25·304

106. *Hydrindene*, C_9H_{10}.

Two specimens were examined, one derived from coal-tar and the other synthetically prepared.

I. From Krämer and Spilker, distilled three times from sodium. Boiling point 176—176·5°.

Relative density:

d 4° = 0·9656. d 10° = 0·9606. d 20° = 0·9536.
d 5 = 0·9646. d 15 = 0·9570. d 25 = 0·9507.

II. Synthetically prepared (W. H. Perkin, jun., Trans., 1894, **65**, 248); it boiled at 176·5—177·5°.

Relative density:

d 4° = 0·9732. d 10° = 0·9681. d 20° = 0·9601.
d 5 = 0·9723. d 15 = 0·9645. d 25 = 0·9582.

107. *Indene*, C_9H_8.

Three specimens of this hydrocarbon were used, namely, two obtained from coal-tar and one synthetically from hydrindenecarboxylic acid, obtained by W. H. Perkin, jun. As the results were not identical, the numbers obtained with each specimen are given.

I. From coal-tar, from Krämer and Spilker, fractionated three times from sodium. Boiling point 179·5—180·5° (corr.).

Relative density:

d 4° = 1·0277. d 10° = 1·0225. d 20° = 1·0152.
d 5 = 1·0268. d 15 = 1·0187. d 25 = 1·0121.

II. From coal-tar, but purified as picrate, distilled over sodium. Boiling point 177—178·5° (corr.).

Relative density:

d 4° = 1·0479. d 10° = 1·0427. d 20° = 1·0350.
d 5 = 1·0470. d 15 = 1·0387. d 25 = 1·0318.

III. From coal-tar, Fabrik Erkner. Boiling point 176—178° (corr.).

Relative density:

d 4° = 1·0600. d 10° = 1·0548. d 20° = 1·0473.
d 5 = 1·0590. d 15 = 1·0509. d 25 = 1·0439.

From the results obtained, there is evidently a good deal of variation in the samples, as shown in the following table.

Boiling point.	d 15°/15°.	Mol. rotation.	Average.
I. 180·0°	1·0187	15·355	15·350
II. 177·8	1·0387	15·255	15·253
III. 177·0	1·0509	14·946	14·946
		t = 17·7	15·183
			0·017
	Average ..	15·0°	15·200

IV. Synthetical indene from the barium salt of hydrindenecarboxylic acid (W. H. Perkin, jun., Trans., 1894, **65**, 246), boiling at 181°. Mol. rotation 16·202.

Relative density:

d 4° = 1·0059.
d 5 = 1·0050.
d 10° = 1·0008.
d 15 = 0·9971.
d 20° = 0·9925.
d 25 = 0·9906.

It is evident that there is a difference either in purity or of constitution in the indene from the two sources. The synthetical is, no doubt, a pure compound.

Aromatic Alcohols, Aldehydes, and Ketones.

108. *Benzylic Alcohol*, $C_7H_8O = C_6H_5\cdot CH_2\cdot OH$ (b. p. 205·2—205·4°).

Relative density:

d 4° = 1·0579.
d 5 = 1·0572.
d 10 = 1·0534.
d 15 = 1·0500.
d 20 = 1·0469.
d 25 = 1·0441.
d 30 = 1·0416.
d 35° = 1·0394.
d 40 = 1·0374.
d 45 = 1·0355.
d 50 = 1·0338.
d 55 = 1·0322.
d 60 = 1·0306.
d 65 = 1·0292.
d 70° = 1·0278.
d 75 = 1·0265.
d 80 = 1·0255.
d 85 = 1·0245.
d 90 = 1·0237.
d 95 = 1·0230.
d 100 = 1·0225.

109. *Cuminic Alcohol*, $C_{10}H_{14}O = C_3H_7\cdot C_6H_5\cdot CH_2OH$.

After fractionating several times, it boiled at 248·4—248·9° (corr.).

Relative density:

d 4° = 0·9869.
d 5 = 0·9863.
d 10 = 0·9834.
d 15 = 0·9805.
d 20 = 0·9777.
d 25 = 0·9753.
d 30 = 0·9733.
d 35° = 0·9713.
d 40 = 0·9696.
d 45 = 0·9677.
d 50 = 0·9661.
d 55 = 0·9646.
d 60 = 0·9632.
d 65 = 0·9620.
d 70° = 0·9609.
d 75 = 0·9600.
d 80 = 0·9592.
d 85 = 0·9585.
d 90 = 0·9579.
d 95 = 0·9576.
d 100 = 0·9572.

110. *Methylsaligenin*, $C_8H_{10}O_2 = CH_3O\cdot C_6H_4\cdot CH_2\cdot OH$.

This was prepared by dissolving saligenin in methylic alcohol in which the necessary amount of sodium had been dissolved, adding methylic iodide, and then heating the mixture in a soda-water bottle for four or five hours at 100°. The alcohol and excess of iodide were afterwards distilled off, water and ether added, and the ethereal solution washed with alkali; after removal of the ether, the residue was distilled under a pressure of 250 mm., about half coming over at 180—184°, the temperature then gradually rising until it reached 300°. The first portion, on being fractionated a few times, boiled constantly at 180° under a pressure of 250 mm.

Relative density:
d 4° = 1·0585. *d* 10° = 1·0534. *d* 20° = 1·0459.
d 5 = 1·0576. *d* 15 = 1·0495. *d* 25 = 1·0427.

111. *Anisic Alcohol*, $C_8H_{10}O_2 = CH_3O{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$.

Prepared from anisaldehyde by means of alcoholic potash, the alcohol obtained being treated a second time with alcoholic potash to ensure the removal of every trace of the aldehyde; 60 grams of anisaldehyde yielded about 20 grams of the alcohol. It boiled at 215—217°, and when treated with sodium hydrogen sulphite did not show the presence of any unchanged aldehyde. When kept it solidified, the freezing point being about 17°; Cannizzaro and Körner (*Ber.*, 1872, **5**, 436) give its melting point as 25°; but Biedermann (*Ber.*, 1886, **19**, 2376), who prepared it from parahydroxybenzylic alcohol by the action of methylic iodide and caustic potash, gives it as 45°. This large difference would indicate the possibility of the latter being an isomeric compound.

Relative density:
d 4° = 1·1202. *d* 10° = 1·1160. *d* 20° = 1·1102.
d 5 = 1·1195. *d* 15 = 1·1129. *d* 25 = 1·1076.

112. *Benzaldehyde*, $C_7H_6O = C_6H_5{\cdot}COH$.

The natural product was employed for examination. Boiling point 178·6—178·9°.

Relative density:
d 4° = 1·0591. *d* 35° = 1·0379. *d* 70° = 1·0228.
d 5 = 1·0582. *d* 40 = 1·0354. *d* 75 = 1·0211.
d 10 = 1·0539. *d* 45 = 1·0330. *d* 80 = 1·0195.
d 15 = 1·0500. *d* 50 = 1·0308. *d* 85 = 1·0181.
d 20 = 1·0466. *d* 55 = 1·0286. *d* 90 = 1·0169.
d 25 = 1·0434. *d* 60 = 1·0266. *d* 95 = 1·0157.
d 30 = 1·0406. *d* 65 = 1·0247. *d* 100 = 1·0147.

113. *Cuminaldehyde*, $C_{10}H_{12}O = C_3H_7{\cdot}C_6H_4{\cdot}COH$.

This was purified by conversion into the sodium hydrogen sulphite compound, which was well washed with alcohol and dried; it was then decomposed with dilute sulphuric acid, the aldehyde mixed with ether, washed with dilute potash, dried, and distilled. It boiled constantly at 235·5° (corr.).

Relative density:
d 4° = 0·9898. *d* 10° = 0·9851. *d* 20° = 0·9787.
d 5 = 0·9889. *d* 15 = 0·9818. *d* 25 = 0·9759.

114. *Anisaldehyde*, $C_8H_8O_2 = CH_3O{\cdot}C_6H_4{\cdot}CO_2H$.

Prepared from the potassium hydrogen sulphite compound by decomposing it with dilute sulphuric acid. It boiled at 199—199·5° under a pressure of 210 mm., and at 248° (corr.). Cooled in ice and salt, it solidified, and a thermometer placed in the melting product remained constant at —0·02°.

Relative density:

d 4° = 1·1343. *d* 10° = 1·1295. *d* 20° = 1·1227.
d 5 = 1·1336. *d* 15 = 1·1260. *d* 25 = 1·1197.

115. *Methylsalicylic Aldehyde*, $C_8H_8O_2 = CH_3O{\cdot}C_6H_4{\cdot}COH$.

This was prepared from the pure sodium compound of salicylic aldehyde by the action of methylic iodide in the presence of methylic alcohol. It was then steam distilled, dissolved in ether, washed with dilute potash, dried and distilled, most of it coming over at 243—244°. On cooling, it solidified and the crystalline mass was well pressed between bibulous paper; it then distilled at 243° (corr.), and at 199° under a pressure of 250 mm., coming over as a colourless oil as previously stated. (Trans., 1889, **55**, 550.) This substance has two fusing points, one at 2·7—3°, and the other at 35°.

Relative density:

d 4° = 1·1445. *d* 10° = 1·1392. *d* 20° = 1·1319.
d 5 = 1·1436. *d* 15 = 1·1354. *d* 25 = 1·1287.

116. *Salicylaldehyde*, $C_7H_6O_2 = HO{\cdot}C_6H_4{\cdot}COH$.

This was prepared by the oxidation of salicin (b. p. 197°, corr.).

Relative density:

d 4° = 1·1626. *d* 10° = 1·1571. *d* 20° = 1·1495.
d 5 = 1·1617. *d* 15 = 1·1530. *d* 25 = 1·1461.

117. *Acetophenone*, $C_8H_8O = C_6H_5{\cdot}CO{\cdot}CH_3$.

Kahlbaum's acetophenone was cooled so as to crystallise it, and the solid mass thoroughly drained, and rubbed between bibulous paper until free from oil. It then boiled at 202° (corr.). The fused product often remains liquid below its fusing point for a considerable time.

Relative density:

d 5° = 1·0408. *d* 20° = 1·0296. *d* 40° = 1·0184.
d 7 = 1·0391. *d* 25 = 1·0266. *d* 45 = 1·0161.
d 10 = 1·0367. *d* 30 = 1·0237. *d* 50 = 1·0140.
d 15 = 1·0329. *d* 35 = 1·0210. *d* 55 = 1·0121.

118. *Benzophenone*, $C_{13}H_{10}O = C_6H_5{\cdot}CO{\cdot}C_6H_5$ (b. p. 306·1°).

Relative density:

d 50° = 1·0976. d 70° = 1·0923. d 90° = 1·0898.
d 55 = 1·0961. d 75 = 1·0913. d 95 = 1·0897.
d 60 = 1·0948. d 80 = 1·0905.
d 65 = 1·0935. d 85 = 1·0901.

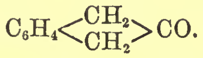
119. *Phenyl Ethyl Ketone*, $C_9H_{10}O = C_6H_5{\cdot}CO{\cdot}C_2H_5$.

The product obtained from Kahlbaum was distilled and cooled in a freezing mixture of ice and salt in which it solidified; it was then placed on a porous plate and well broken up and rubbed against it with a pestle until it became a dry white powder. It boiled at 142—142·2° under a pressure of 78 mm. giving a colourless distillate; if left undisturbed it will remain liquid for days, but the introduction of a trace of the solid product causes it to solidify quickly.

Relative density:

d 15° = 1·0150. d 20° = 1·0118. d 25° = 1·0087.

120. *α-Hydrindone*, C_9H_8O =



$C_6H_4\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle CO$.

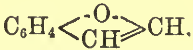
Dr. Kipping was kind enough to furnish me with this substance. Its melting point was 42°.

Relative density:—

d 40° = 1·1028. d 55° = 1·0977. d 70° = 1·0934.
d 45 = 1·1011. d 60 = 1·0962. d 75 = 1·0921.
d 50 = 1·0993. d 65 = 1·0947. d 80 = 1·0908.

When examined for magnetic rotation in the measuring tube, this specimen was rather strongly coloured, of a brownish-orange shade, and oxygen had to be used with the sodium light in order to get a light sufficiently intense for the measurements.

121. *Coumarone*, C_8H_6O =



$C_6H_4\left\langle\begin{matrix}O\\CH\end{matrix}\right\rangle CH$.

This was the coal-tar product and obtained from the Fabrik Erkner. It boiled at 173—175° (corr.).

Relative density:—

d 4° = 1·0870. d 10° = 1·0816. d 20° = 1·0740.
d 5 = 1·0860. d 15 = 1·0776. d 25 = 1·0705.

HALOGEN DERIVATIVES, &c., OF AROMATIC HYDROCARBON.

122. *Fluorobenzene*, C_6H_5Fl.

For the use of the specimen of this substance examined, I am indebted to Dr. Sydney Young. Boiling point 85° (corr.).

Relative density:—

d 4° = 1·0418.
d 5 = 1·0404.
d 10° = 1·0343.
d 15 = 1·0290.
d 20° = 1·0244.
d 25 = 1·0200.

123. *Chlorobenzene*, C_6H_5Cl.

Prepared from aniline by Sandmeyer's process. It was purified by three treatments with concentrated sulphuric acid, until the latter was only coloured yellow by it; and then after washing with water it was treated several times with potash until the latter was no longer coloured; when dried it was distilled from phosphoric anhydride. Boiling point 131·4—131·6° (corr.).

Relative density:

d 4° = 1·1230.
d 5 = 1·1220.
d 10 = 1·1171.
d 15 = 1·1125.
d 20 = 1·1082.
d 25 = 1·1042.
d 30 = 1·1004.
d 35° = 1·0969.
d 40 = 1·0934.
d 45 = 1·0900.
d 50 = 1·0868.
d 55 = 1·0837.
d 60 = 1·0809.
d 65 = 1·0782.
d 70° = 1·0755.
d 75 = 1·0728.
d 80 = 1·0702.
d 85 = 1·0678.
d 90 = 1·0658.
d 95 = 1·0640.
d 100 = 1·0623.

124. *Paradichlorobenzene*, $C_6H_4Cl_2$.

This specimen examined boiled at 173·7° (corr.). Its freezing point was 53·2°.

Relative density:

d 55° = 1·2675.
d 60 = 1·2648.
d 65 = 1·2623.
d 70° = 1·2600.
d 75 = 1·2580.
d 80 = 1·2562.
d 90° = 1·2545.

125. *Bromobenzene*, C_6H_5Br.

This was prepared like the chlorobenzene by Sandmeyer's process and purified in the same manner; as, however, it was not perfectly homogeneous it was fractionated several times. A second specimen was then made from the pure potassium parabromobenzenesulphonate by hydrolysis; after distillation, even this was not quite pure, the first and last fractions differing in density by 0·0015. This was also fractionated repeatedly. The two preparations were mixed for use. Boiling point 155·0° (corr.).

Relative density:

d 4° = 1·5103.
d 5 = 1·5092.
d 10 = 1·5042.
d 15 = 1·4991.
d 20 = 1·4936.
d 25 = 1·4886.
d 30 = 1·4841.
d 35° = 1·4798.
d 40 = 1·4758.
d 45 = 1·4718.
d 50 = 1·4681.
d 55 = 1·4648.
d 60 = 1·4613.
d 65 = 1·4582.
d 70° = 1·4552.
d 75 = 1·4522.
d 80 = 1·4494.
d 85 = 1·4468.
d 90 = 1·4447.
d 95 = 1·4430.
d 100 = 1·4416.

126. *Iodobenzene*, C_6H_5I.

The substance used was obtained from Kahlbaum, but although it boiled within a fraction of a degree, on taking the density of the first and last fractions a variation of 0·0025 was found. After being refractionated a great many times until the density of the first and last fractions varied by only about 0·0007, it was once more distilled, the first and last portions being rejected. The boiling point was 187·7° (corr.).

Relative density:

d 4° = 1·8551. d 35° = 1·8175. d 70° = 1·7944.
d 5 = 1·8534. d 40 = 1·8136. d 75 = 1·7920.
d 10 = 1·8462. d 45 = 1·8100. d 80 = 1·7899.
d 15 = 1·8401. d 50 = 1·8067. d 85 = 1·7879.
d 20 = 1·8341. d 55 = 1·8032. d 90 = 1·7862.
d 25 = 1·8283. d 60 = 1·8000. d 95 = 1·7847.
d 30 = 1·8239. d 65 = 1·7971. d 100 = 1·7832.

127. *Orthochlorotoluene*, $CH_3{\cdot}C_6H_4Cl$ (b. p. 159—159·2° corr.).

Relative density:

d 4° = 1·0973. d 10° = 1·0918. d 20° = 1·0837.
d 5° = 1·0963. d 15 = 1·0877. d 25° = 1·0801.

128. *Parachlorotoluene*, $CH_3{\cdot}C_6H_4Cl$.

Solidifying point 7·4°. Boiling point 162—162·2° (corr.).

Relative density:

d 4° = 1·0847. d 10° = 1·0791. d 20° = 1·0710.
d 5 = 1·0836. d 15° = 1·0749. d 25° = 1·0672.

129. *Benzylic Chloride*, $C_6H_5{\cdot}CH_2Cl$.

This was prepared from benzylic alcohol by means of hydrogen chloride. It was first steam distilled, and then twice fractionated. Most of it came over at 179° (corr.), as a colourless oil.

Relative density:

d 4° = 1·1135. d 10° = 1·1081. d 20° = 1·1002.
d 5 = 1·1125. d 15 = 1·1040. d 25 = 1·0967.

130. *Orthobromotoluene*, $CH_3{\cdot}C_6H_4Br$.

The specimen examined was obtained through the kindness of Dr. A. K. Miller, who prepared it by the hydrolysis of the pure sulphonic acid. When fractionated, the first and last portions differed in density by about 0·0004. Boiling point 181° (corr.).

Relative density:

d 4° = 1·4437.
d 5 = 1·4424.
d 10° = 1·4362.
d 15 = 1·4309.
d 20° = 1·4264.
d 25 = 1·4222.

131. *Parabromotoluene*, $CH_3{\cdot}C_6H_4Br$ (b. p. 183·8°, corr.).

Relative density:

d 35° = 1·3959.
d 40 = 1·3921.
d 45 = 1·3887.
d 50 = 1·3856.
d 55 = 1·3826.
d 60° = 1·3799.
d 65 = 1·3772.
d 70 = 1·3746.
d 75 = 1·3722.
d 80 = 1·3699.
d 85° = 1·3679.
d 90 = 1·3662.
d 95 = 1·3648.
d 100 = 1·3637.

132. *Phenylic Sulphide*, $S(C_6H_5)_2$.

Mr. C. E. Groves kindly supplied me with a quantity of the product which he had prepared in the late Dr. Stenhouse's laboratory by the distillation of sodium benzenesulphonate. After a large number of fractionations, the phenylic sulphide was obtained, boiling at 296—297° (corr.).

Relative density:

d 4° = 1·1266.
d 5 = 1·1258.
d 10 = 1·1221.
d 15 = 1·1185.
d 20 = 1·1153.
d 25 = 1·1125.
d 30 = 1·1099.
d 35° = 1·1076.
d 40 = 1·1054.
d 45 = 1·1035.
d 50 = 1·1017.
d 55 = 1·1002.
d 60 = 1·0987.
d 65 = 1·0975.
d 70° = 1·0963.
d 75 = 1·0953.
d 80 = 1·0944.
d 85 = 1·0937.
d 90 = 1·0931.
d 95 = 1·0927.
d 100 = 1·0924.

133. *Thiophen*, C_4H_4S.

Distilled from phosphoric anhydride. This substance boiled constantly at 84°.

Relative density:

d 4° = 1·0828.
d 5 = 1·0819.
d 10° = 1·0764.
d 15 = 1·0708.
d 20° = 1·0658.
d 25 = 1·0615.

134. *Benzylic Sulphide*, $C_{14}H_{14}S = S(CH_2{\cdot}C_6H_5)_2$.

Relative density:

d 50° = 1·0712.
d 55 = 1·0698.
d 60 = 1·0685.
d 65 = 1·0673.
d 70° = 1·0662.
d 75 = 1·0653.
d 80 = 1·0644.
d 85 = 1·0639.
d 90° = 1·0635.
d 95 = 1·0634.
d 100 = 1·0634.

135. *Thiocarbanil, Phenyl Mustard Oil*, $C_7H_5N{\cdot}S{\cdot}C_6H_5NCS$. (Boiling point 221° (corr.).

Relative density:

d 4° = 1·1477.
d 5 = 1·1467.
d 10° = 1·1421.
d 15 = 1·1382.
d 20° = 1·1346.
d 25 = 1·1314.

136. *Benzenesulphonic Chloride*, $C_6H_5{\cdot}SOCl$ (b. p. 251·5°, corr.).

Relative density:

d 4° = 1·3949.   *d* 10° = 1·3887.   *d* 20° = 1·3803.
d 5 = 1·3939.   *d* 15 = 1·3842.   *d* 25 = 1·3766.

137. *Benzoic Chloride*, $C_7H_5OCl = C_6H_5{\cdot}COCl$.

This was fractionated several times, and then kept in several small bottles for use, a fresh bottle being opened for each examination of its density or rotation. Boiling point 197·2° (corr.).

Relative density:

d 4° = 1·2291.   *d* 10° = 1·2231.   *d* 20° = 1·2146.
d 5 = 1·2281.   *d* 15 = 1·2187.   *d* 25 = 1·2112.

138. *Phthalic Chloride*, $C_8H_4O_2Cl_2$ (b. p. 281—281·2°, corr.).

Relative density:

d 4° = 1·4323.   *d* 10° = 1·4260.   *d* 20° = 1·4172.
d 5 = 1·4312.   *d* 15 = 1·4214.   *d* 25 = 1·4135.

139. *Phenylacetic or α-Toluic Chloride*, $C_8H_7OCl = C_6H_5{\cdot}CH_2{\cdot}COCl$.

When fractionated under reduced pressure a few times, it was obtained boiling very constantly at 170° under a pressure of 250 mm.

Relative density:

d 4° = 1·1856.   *d* 10° = 1·1798.   *d* 20° = 1·1712.
d 5 = 1·1846.   *d* 15 = 1·1753.   *d* 25° = 1·1674.

140. *Metachloraniline*, $C_6H_6ClN = C_6H_4Cl{\cdot}NH_2$.

This base, after a few fractionations, boiled at 236·5°.

Relative density:

d 4° = 1·2317.   *d* 35° = 1·2102.   *d* 70° = 1·1973.
d 5 = 1·2307.   *d* 40 = 1·2079.   *d* 75 = 1·1960.
d 10 = 1·2265.   *d* 45 = 1·2058.   *d* 80 = 1·1951.
d 15 = 1·2225.   *d* 50 = 1·2038.   *d* 85 = 1·1943.
d 20 = 1·2191.   *d* 55 = 1·2019.   *d* 90 = 1·1938.
d 25 = 1·2158.   *d* 60 = 1·2002.   *d* 95 = 1·1933.
d 30 = 1·2129.   *d* 65 = 1·1987.   *d* 100 = 1·1930.

141. *Parachloraniline*, $C_6H_6ClN = C_6H_4Cl{\cdot}NH_2$.

This boiled constantly at 232·3° (corr.), and crystallised rapidly on cooling. The boiling points of this and of the meta-compound were determined at the same time and with the same thermometer, and show a difference of 4·2°.

Relative density:

d 70° = 1·1970.
d 75 = 1·1958.
d 80 = 1·1948.
d 85° = 1·1940.
d 90 = 1·1936.
d 95 = 1·1931.
d 100° = 1·1928.

142. *Benzonitrile*, $C_7H_5N = C_6H_5{\cdot}CN$ (b. p. 190·7°, corr.).

Relative density:

d 4° = 1·0191.
d 5 = 1·0181.
d 10° = 1·0140.
d 15 = 1·0102.
d 20° = 1·0066.
d 25 = 1·0036.

143. *Paratoluonitrile*, $C_8H_7N = CH_3{\cdot}C_6H_4{\cdot}CN$.

Boiling point 217·6°. Solidifying point 27·5°.

Relative density:

d 30° = 0·9805.
d 35 = 0·9780.
d 40° = 0·9763.
d 45 = 0·9751.

No temperature differences of compounds of this kind have been determined. Its specific rotation, however, is close to that of benzaldehyde, and probably the difference will not be far from that of this substance, namely, 0·379 for 100°. This has therefore been applied in this case to reduce the rotation to 15·0°.

144. *Orthotolunitrile*, $C_8H_7N = CH_3{\cdot}C_6H_4{\cdot}CN$ (b. p. 205·2°, corr.).

Relative density:

d 4° = 1·0061.
d 5 = 1·0052.
d 10° = 1·0012.
d 15 = 0·9975.
d 20° = 0·9942.
d 25 = 0·9912.

145. *Benzylic Cyanide*, $C_8H_7N = C_6H_5{\cdot}CH_2{\cdot}CN$ (b. p. 233—234°).

Relative density:

d 4° = 1·0296.
d 5 = 1·0288.
d 10° = 1·0249.
d 15 = 1·0214.
d 20° = 1·0183.
d 25 = 1·0154.

146. *α-Naphthonitrile*, $C_{11}H_7N = C_{10}H_7{\cdot}CN$.

The substance, as obtained from Kahlbaum, was solid, but when very strongly pressed, a small quantity of oily product was separated. It was then a hard, porcelain-like mass, which melted at 35—36°, and boiled at 299° (corr.). After being fused, it remains in a state of surfusion for a long time.

Relative density:

d 4° = 1·1243.
d 5 = 1·1235.
d 10° = 1·1199.
d 15 = 1·1167.
d 20° = 1·1138.
d 25 = 1·1113.

147. *β-Naphthonitrile*, $C_{11}H_7 = C_{10}H_7{\cdot}CN$.

This boiled at 306·5°, or 7·5° higher than the α-compound. The boiling points given in Beilstein make the difference 7·0°. It came over as a colourless oil, solidifying to a porcelain-looking mass. It commenced solidifying at 56·9°, but the temperature gradually rose to 59·0°.

Relative density:

d 60° = 1·0939. *d* 75° = 1·0921. *d* 90° = 1·0905.
d 65 = 1·0933. *d* 80 = 1·0916. *d* 95 = 1·0901.
d 70 = 1·0927. *d* 85 = 1·0910.

Magnetic rotation three times determined.

	t.	Sp. rotation.	Mol. rotation.
	71·2°	3·3178	25·811
Corrected to	15·0 by estimated temp. diff. of	0·453 for 100° ..	26·264

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148. *Aniline*, $C_6H_7N = C_6H_5{\cdot}NH_2$.

The substance examined boiled constantly at 184° (corr.).

Relative density:

d 4° = 1·0342. *d* 25° = 1·0191. *d* 75° = 0·9970.
d 5 = 1·0333. *d* 55 = 1·0038. *d* 80 = 0·9957.
d 10 = 1·0292. *d* 60 = 1·0019. *d* 85 = 0·9943.
d 15 = 1·0254. *d* 65 = 1·0001. *d* 90 = 0·9931.
d 20 = 1·0219. *d* 70 = 0·9985. *d* 95 = 0·9919.

149. *Methylaniline*, $C_7H_9N = C_6H_5{\cdot}NH{\cdot}CH_3$.

This boiled constantly at 195·5° (corr.), or 2·5° higher than dimethylaniline when distilled in the same vessel, and with the same thermometer.

Relative density;

d 4° = 0·9993. *d* 10° = 0·9946. *d* 20° = 0·9882.
d 5 = 0·9984. *d* 15 = 0·9912. *d* 25 = 0·9854.

150. *Dimethylaniline*, $C_8H_{11}N = C_6H_5N(CH_3)_2$ (b. p. 193°, corr.).

Relative density:

d 4° = 0·9703. *d* 35° = 0·9508. *d* 70° = 0·9370.
d 5 = 0·9695. *d* 40 = 0·9484. *d* 75 = 0·9354.
d 10 = 0·9657. *d* 45 = 0·9461. *d* 80 = 0·9340.
d 15 = 0·9621. *d* 50 = 0·9440. *d* 85 = 0·9327.
d 20 = 0·9587. *d* 55 = 0·9421. *d* 90 = 0·9314.
d 25 = 0·9559. *d* 60 = 0·9403. *d* 95 = 0·9302.
d 30 = 0·9534. *d* 65 = 0·9386. *d* 100 = 0·9289.

151. *Ethylaniline*, $C_8H_{11}N = C_6H_5 \cdot NH \cdot C_2H_5$ (b. p. 205—206°).

Relative density:

d 4° = 0·9727. *d* 10° = 0·9678. *d* 20° = 0·9611.
d 5 = 0·9719. *d* 15 = 0·9643. *d* 25 = 0·9583.

152. *Diethylaniline*, $C_{10}H_{15}N = C_6H_5 \cdot N(C_2H_5)_2$ (b. p. 216—216·5°).

Relative density:

d 4° = 0·9471. *d* 10° = 0·9425. *d* 20° = 0·9357.
d 5 = 0·9463. *d* 15 = 0·9389. *d* 25 = 0·9331.

153. *Methyldiphenylamine*, $C_{13}H_{13}N = (C_6H_5)_2N \cdot CH_3$ (b. p. 295·5—296·5°, corr.).

Relative density:

d 4° = 1·0603. *d* 10° = 1·0557. *d* 20° = 1·0491.
d 5 = 1·0596. *d* 15 = 1·0522. *d* 25 = 1·0465.

154. *Benzylamine*, $C_7H_9N = C_6H_5 \cdot CH_2 \cdot NH_2$ (b. p. 184—185°, corr.).

Relative density:

d 4° = 0·9957. *d* 35° = 0·9747. *d* 70° = 0·9394.
d 5 = 0·9948. *d* 40 = 0·9721. *d* 75 = 0·9576.
d 10 = 0·9905. *d* 45 = 0·9698. *d* 80 = 0·9561.
d 15 = 0·9865. *d* 50 = 0·9676. *d* 85 = 0·9549.
d 20 = 0·9832. *d* 55 = 0·9654. *d* 90 = 0·9537.
d 25 = 0·9802. *d* 60 = 0·9633. *d* 95 = 0·9527.
d 30 = 0·9774. *d* 65 = 0·9612. *d* 100 = 0·9518.

155. *Mixture of Benzylamine and Water, equal volumes, at* 15°. Composition = $C_7H_9N + 6{\cdot}022H_2O$.

Calculated relative density: *d* 15° = 0·9935. Found: 1·0093. Diff.: 0·0101 (contraction).

Magnetic rotation:

	t.	Sp. rotation.	Mol. rotation.	Diff.
Unmixed....	15·0°	1·6389	19·739	0·585
Mixed......	,,	1·6157	19·154	
		Calculated......	19·687	

156. *Dibenzylamine*, $C_{14}H_{15}N = NH(C_6H_5 \cdot CH_2)_2$.

This specimen, which was obtained from Schuchardt, contained some tribenzylamine, which was separated by distillation under reduced pressure. The specimen examined boiled at 268—271° under a pressure of 250 mm.

Relative density:

d 4° = 1·0415. *d* 10° = 1·0370. *d* 20° = 1·0306.
d 5 = 1·0407. *d* 15 = 1·0336. *d* 25 = 1·0281.

157. *Benzylaniline*, $C_{13}H_{13}N = C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5$.

This base remains liquid for a considerable time, at a temperature many degrees below its melting point (32°). Advantage was taken of this in the following determinations.

Relative density:

d 15° = 1·0698.	*d* 25° = 1·0647.	*d* 35° = 1·0601.
d 20 = 1·0672.	*d* 30 = 1·0622.	

158. *Phenylazoimide*, $C_6H_5N_3$.

For the specimen of this substance I am indebted to Dr. Tilden.

Relative density:

d 10° = 1·0980.	*d* 20° = 1·0880.
d 15 = 1·0932.	*d* 25 = 1·0853.

159. *Phenylhydrazine*, $C_6H_8N_2 = C_6H_5{\cdot}NH{\cdot}NH_2$.

This boiled constantly at 243·5°, distilling as a nearly colourless oil. It could be kept in a liquid condition for some time at a temperature considerably below its melting point.

Relative density:

d 10° = 1·1070.	*d* 20° = 1·0994.
d 15 = 1·1027.	*d* 25 = 1·0970.

160. *Paratoluidine*, $C_7H_9N = CH_3{\cdot}C_6H_4{\cdot}NH_2$.

This base was purified by crystallisation from a small quantity of alcohol, the crystals being strongly pressed in calico, and then pressed on a porous plate; they were quite white, and, when distilled, boiled constantly at 200·3° (corr.).

Another specimen, recently obtained from Kahlbaum, boiled at 200·5°, and had a solidifying point of 42·8°.

Relative density:

d 50° = 0·9730.	*d* 60° = 0·9692.	*d* 70° = 0·9670.
d 55 = 0·9707.	*d* 65 = 0·9679.	

To examine paratoluidine at ordinary temperatures, it was dissolved in its own weight of orthotoluidine.

Relative density: *d* 10° = 1·0009. *d* 15° = 0·9973.

Magnetic rotation:

t.	Sp. rotation.	Mol. rotation.
16·2°	2·7985	33·388
	Orthotoluidine at 16·2°	17·192
		16·196
	Corrected to 15·0°	16·188

Solution of Paratoluidine in Alcohol.

This solution was made in the proportion of 1 mol. of paratoluidine to 2 mols. of absolute alcohol.

Relative density of solution:

$d\ 10° = 0·9041$. $d\ 20° = 0·8974$.
$d\ 15 = 0·9008$. $d\ 25 = 0·8942$.

The magnetic rotation twice determined:

t.	Sp. rotation.	Mol. rotation.
15·0°	1·7130	21·023
	Less rot. of 2 mols. alcohol	5·560
		15·463

In reference to this result see section on Solutions (p. 1058).

161. *Orthotoluidine*, $C_7H_9N = CH_3·C_6H_4·NH_2$.

Orthotoluidine, used for technical purposes, was purified by the process described by Rosenstiehl, namely, by treating its ethereal solution with an ethereal solution of oxalic acid so as to remove any paratoluidine it might contain. It boiled at 199—200° (corr.). Another specimen recently obtained from Kahlbaum boiled at 199·5° (corr.).

Relative density:

$d\ 4° = 1·0112$. $d\ 20° = 0·9998$. $d\ 40° = 0·9896$.
$d\ 5 = 1·0103$. $d\ 25 = 0·9970$. $d\ 45 = 0·9874$.
$d\ 10 = 1·0066$. $d\ 30 = 0·9944$. $d\ 50 = 0·9852$.
$d\ 15 = 1·0031$. $d\ 35 = 0·9919$. $d\ 55 = 0·9851$.

162. *Metatoluidine*, $C_7H_9N = CH_3·C_6H_4·NH_2$.

This was obtained from Schuchardt; when fractionated, rather more than half came over between 206° and 210°. It was afterwards refractionated several times, using a column, and the main portion was then obtained boiling at 203° (corr.), a few drops coming over at 204°. This is a slightly higher boiling point taken in relation to the ortho- and para-toluidines, than that obtained by other observers. The following are the results given in this paper:

Metatoluidine.................	203·0°
Paratoluidine	200·3
Orthotoluidine.................	199·5

Relative density of metatoluidine:

$d\ 4° = 1·0041$. $d\ 10° = 0·9996$. $d\ 20° = 0·9929$.
$d\ 5 = 1·0033$. $d\ 15 = 0·9961$. $d\ 25 = 0·9900$.

163. *Dimethylorthotoluidine*, $CH_3{\cdot}C_6H_4{\cdot}N(CH_3)_2$.

Both this and the para-compound were obtained from Kahlbaum, and their rotations determined after fractionating, and again after they had been treated with acetyl chloride, &c.; this final treatment did not remove anything from them. In both cases the results obtained were practically the same. The boiling point of the dimethylorthotoluidine was 185·5°.

Relative density:

d 4° = 0·9417.
d 5 = 0·9407.
d 10° = 0·9369.
d 15 = 0·9333.
d 20° = 0·9299.
d 25 = 0·9268.

164. *Dimethylparatoluidine*, $CH_3{\cdot}C_6H_4{\cdot}N(CH_3)_2$ (b. p. 211—211·5°, corr.).

Relative density:

d 4° = 0·9502.
d 5 = 0·9495.
d 10° = 0·9459.
d 15 = 0·9424.
d 20° = 0·9393.
d 25 = 0·9364.

165. *Orthoanisidine*, $C_7H_9NO = CH_3{\cdot}O{\cdot}C_6H_4{\cdot}NH_2$.

The specimen examined boiled constantly at 225° (corr.), distilling as a colourless oil; this, however, soon became coloured on standing, so that it was necessary to redistil it each time it was examined.

Relative density:

d 4° = 1·1062.
d 5 = 1·1054.
d 10 = 1·1016.
d 15 = 1·0978.
d 20 = 1·0945.
d 25 = 1·0914.
d 30 = 1·0885.
d 35° = 1·0857.
d 40 = 1·0832.
d 45 = 1·0808.
d 50 = 1·0788.
d 55 = 1·0768.
d 60 = 1·0751.
d 65 = 1·0736.
d 70° = 1·0723.
d 75 = 1·0711.
d 80 = 1·0702.
d 85 = 1·0694.
d 90 = 1·0686.

166. *Para-anisidine*, C_7H_9NO.

Boiling point 243° (corr.), or 18° above that of the ortho-compound. Solidifying point 57·2°.

Relative density:

d 55° = 1·0866.
d 60 = 1·0846.
d 65 = 1·0829.
d 70° = 1·0816.
d 75 = 1·0806.
d 80 = 1·0798.
d 85° = 1·0791.
d 90 = 1·0786.

167. *α-Naphthylamine.*

This was distilled in a current of carbonic anhydride, and the colourless distillate cooled in the gas, when it solidified to a white, crystalline mass. It often remains in a state of surfusion much below its solidifying point. The boiling point was 300·8°.

Relative density:

d 25° = 1·1229.
d 30 = 1·1210.
d 35 = 1·1192.
d 40 = 1·1175.
d 45 = 1·1158.
d 50 = 1·1144.
d 55° = 1·1131.
d 60 = 1·1120.
d 65 = 1·1112.
d 70 = 1·1104.
d 75 = 1·1098.
d 80 = 1·1093.
d 85° = 1·1091.
d 90 = 1·1091.
d 95 = 1·1093.
d 100 = 1·1098.

168. *β-Naphthylamine.*

A fused mixture of equal weights of *α*- and *β*-naphthylamine was used, as the *β*-compound melts at too high a temperature for examination (111—112°). The bases had to be freshly distilled in hydrogen in order to obtain the mixture sufficiently free from colour, and also melted in an atmosphere of this gas before being transferred to the measuring tube. This mixture was found very troublesome to examine on account of the readiness with which it became coloured when kept at its fusing point; this is the reason it was only once examined, although several attempts were made to repeat the measurements. It would be desirable to re-examine this mixture several times, and then take the average; the following results, however, are probably near the truth. Boiling point 306·1°.

Relative density of the mixture:

d 80° = 1·1041. *d* 90° = 1·1046.

Magnetic rotation:

t.	Sp. rotation.	Mol. rotation.
82·3°	4·9351	71·078
	Less *α*-naphthylamine at 82·3°	36·428
	β-naphthylamine at 82·3	34·650
	Corrected to 15·0° (by temp. diff. of *α*-naphthylamine)	35·700

169. *Dimethyl-β-naphthylamine*, $C_{12}H_{13}N = C_{10}H_7 \cdot N(CH_3)_2$.

Obtained from Schuchardt. It boiled at 212—214°, mostly at 212—213° under a pressure of 69 mm. Its solidifying point was 41° rising to 42°. When distilled under the ordinary pressure in hydrogen, it usually came over a little coloured; if a little caustic potash, however, be previously added it is obtained colourless. It has a blue fluorescence.

Relative density:

d 40° = 1·0455.
d 45 = 1·0442.
d 50 = 1·0430.
d 55° = 1·0419.
d 60 = 1·0407.
d 65 = 1·0397.
d 70° = 1·0387.

Magnetic rotation three times determined :

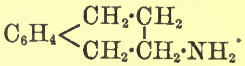
t.	Sp. rotation.	Mol. rotation.
49·4°	5·1436	46·840
Corrected to 15·0° by temp. diff. of α-naphthylamine		47·377

170. *Dimethyl-α-naphthylamine*, $C_{12}H_{13}N = C_{10}H_7 \cdot N(CH_3)_2$.

Obtained from Schuchardt. It distilled mostly at 184—185° under a pressure of 69 mm. When fractionated under a pressure of 90 mm., it nearly all came over at 193° as a colourless liquid with a blue fluoresence. It did not give crystalline salts with acids.

Relative density :

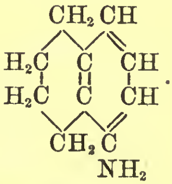
d 4° = 1·0522.
d 5 = 1·0513.
d 10 = 1·0479.
d 15 = 1·0446.
d 20 = 1·0418.
d 25° = 1·0391.
d 30 = 1·0367.
d 35 = 1·0345.
d 40 = 1·0326.
d 45 = 1·0308.
d 50° = 1·0291.
d 55 = 1·0276.
d 60 = 1·0264.
d 65 = 1·0253.
d 70 = 1·0243.

171. ac-*Tetrahydro-β-naphthylamine*, $C_{10}H_{13}N =$ 
$C_6H_4 < \begin{matrix} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \cdot NH_2 \end{matrix}$.

The specimen, obtained from Schuchardt, was fractionated under a pressure of 250 mm. ; from a little sodium most of it distilled at 210° (corr.) as a colourless, rather thick oil.

Relative density :

d 4° = 1·0421.
d 5 = 1·0412.
d 10° = 1·0377.
d 15 = 1·0344.
d 20° = 1·0313.
d 25 = 1·0288.

172. ar-*Tetrahydro-α-naphthylamine*, $C_{10}H_{13}N =$ 

This was obtained from Schuchardt. When fractionated from sodium under a pressure of 250 mm., about half came over at 233—235° (corr.) as a thick oil, the rest of the product being of higher boiling point, and probably containing a little α-naphthylamine. It soon became somewhat coloured on keeping.

Relative density :

d 4° = 1·0746.
d 5 = 1·0738.
d 10° = 1·0702.
d 15 = 1·0668.
d 20° = 1·0640.
d 25 = 1·0616.

173. *Pyridine*, C_5H_5N (b. p. 116·2—116·7°).

Relative density:

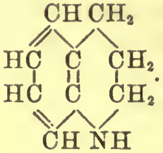
d 4° = 0·9944. *d* 10° = 0·9895. *d* 20° = 0·9816.
d 5 = 0·9935. *d* 15 = 0·9855. *d* 25 = 0·9778.

174. *Quinoline*, C_9H_7N (b. p. 238°, corr.).

Relative density:

d 4° = 1·1063. *d* 10° = 1·1018. *d* 20° = 1·0955.
d 5 = 1·1055. *d* 15 = 1·0985. *d* 25 = 1·0930.

175. *Tetrahydroquinoline*, $C_9H_{11}N$ =



Boiling point 251° (corr.).

Relative density:

d 4° = 1·0704. *d* 10° = 1·0660. *d* 20° = 1·0598.
d 5 = 1·0695. *d* 15 = 1·0627. *d* 25 = 1·0571.

176. *Metaphenylenediamine*, $C_6H_6N_2 = C_6H_4(NH_2)_2$.

This was prepared from the hydrochloride by distillation with lime; when fractionated, most of it passed over at 282—284° (corr.), For examination it was redistilled in hydrogen, when it was obtained colourless. When first prepared, it remained as a thick oil for about a week, but after several distillations its tendency to become solid increased; this was especially the case when it was distilled with caustic potash. It became coloured very quickly on exposure to the air.

Relative density:

d 10° = 1·1421. *d* 30° = 1·1316. *d* 50° = 1·1257.
d 15 = 1·1389. *d* 35 = 1·1298. *d* 55 = 1·1248.
d 20 = 1·1361. *d* 40 = 1·1283. *d* 60 = 1·1240.
d 25 = 1·1337. *d* 45 = 1·1269.

177. *Orthophenylenediamine*, $C_6H_8N_2 = C_6H_4(NH_2)_2$.

This was prepared from Kahlbaum's hydrochloride, by adding caustic potash of sp. gr. 1·27 in excess to its *saturated* solution, when most of the base separated in the solid state; it was collected on a cotton filter and pressed. The aqueous filtrate was treated with ether, and in this way a small additional quantity of base was obtained. The base thus prepared boiled at 256—258° (corr.), most of the product distilling at the latter temperature; Griess gives the boiling point as

252°. It was then rectified in an atmosphere of carbonic anhydride, when it came over as a colourless oil, quickly solidifying to a crystalline mass. As its melting point is above 100°, its magnetic rotation could not be determined when in the pure state, but it was found possible to keep it liquid by mixing it with aniline in the proportion of 1½ mol. of the latter to one of the diamine, and keeping the mixture at a temperature of about 70°. Much trouble, however, was caused by the ready way in which this mixture becomes coloured when heated to this temperature; in fact, it was only found possible to obtain it sufficiently pale in colour for the measurement of its magnetic rotation by performing all the operations in an atmosphere of carbonic anhydride, and also keeping it protected with this in the measuring tube. On cooling, most of the diamine crystallised out from this mixture.

Relative density of the mixture:

$$d\ 66° = 1{\cdot}04811. \qquad d\ 76° = 1{\cdot}0458.$$

The magnetic rotation was four times determined. In the first two, the colour was very considerable and the readings very difficult to make; they gave for the molecular rotation 42·251 at 69·3°. The last two were made with two separately prepared mixtures, and owing to greater precaution having been taken these were more easy to read; as these results are considered to be more trustworthy, they alone are taken. They gave

t.	Sp. rotation.	Mol. rotation.
74·4°	3·2017	42·404
Less 1·5 aniline at 74·4°............		23·458
Orthophenylenediamine at 74·4°.....		18·946
Add temp. diff. for aniline for 59·4 ..		0·445
Orthophenylenediamine at 15·0		19·391

178. *Dimethylparaphenylenediamine*, $C_8H_{12}N_2 = NH_2{\cdot}C_6H_4{\cdot}N(CH_3)_2$.

This was prepared from the hydrochloride by dissolving it in a small quantity of water, and adding an excess of strong caustic potash of sp. gr. 1·27; the oily base was then separated, and the aqueous solution treated with ether to recover any dissolved base, which, however, was but little. The base was distilled with a very small amount of solid potash, when it came over as a colourless oil, rapidly turning brown on contact with the air. It boiled at 262·3° (corr.), and, on standing, solidified to a crystalline mass. It was obtained colourless by rectification in an atmosphere of hydrogen; but while transferring it to the measuring tube for the magnetic rotation determinations, even when the tube was filled with carbonic anhydride, it acquired a brownish tint, which obscured much of the light.

Relative density:

d 15° = 1·0414.
d 20 = 1·0383.
d 25 = 1·0357.
d 30 = 1·0332.
d 35 = 1·0310.
d 40 = 1·0291.
d 45° = 1·0272.
d 50 = 1·0255.
d 55 = 1·0240.
d 60 = 1·0226.
d 65 = 1·0214.
d 70 = 1·0204.
d 75° = 1·0192.
d 80 = 1·0184.
d 85 = 1·0176.
d 90 = 1·0168.

179. *Benzamide*, $C_7H_7NO = C_6H_5{\cdot}CO{\cdot}NH_2$.

The only suitable solvent that could be found for the measurement of this substance was phenol containing 1 mol. of water. The solution had the composition $C_7H_7NO + 2(C_6H_6O + H_2O)$ and contained 37·07 per cent. of benzamide.

Relative density: d 15° = 1·0009. d 25° = 1·0950.

Magnetic rotation three times determined:

t.	Sp. rotation.	Mol. rotation.
15·25°	2·2808	39·712
	$2(C_6H_6O + H_2O)$ ..	26·192
		13·520

180. *Formanilide*, $C_7H_7NO = H{\cdot}CO{\cdot}NH{\cdot}C_6H_5$.

This substance, which remains in a state of surfusion for a long time, was examined both below and above its fusing point. It was melted and filtered before use to remove a very minute quantity of infusible product, which made the readings wanting in sensitiveness; even after this, they were not so good as might be wished, especially at the low temperatures.

Relative density:

d 15° = 1·1473.
d 20 = 1·1441.
d 25 = 1·1415.
d 30 = 1·1391.
d 35 = 1·1371.
d 40° = 1·1353.
d 45 = 1·1336.
d 50 = 1·1322.
d 55 = 1·1310.
d 60 = 1·1299.
d 65° = 1·1291.
d 70 = 1·1285.
d 75 = 1·1280.
d 80 = 1·1277.

181. *Acetanilide*, $C_6H_9NO = CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_5$.

This was purified by rapid distillation; it boiled at 304·5—305·5° (corr.). Phenol was found to be the best solvent for this compound, the solution used having the composition $C_8H_9NO + 1{\cdot}5C_6H_6O$; it crystallised on standing.

Relative density of the mixture :

$d\ 67° = 1·07503$. $d\ 77° = 1·0732$.

The determination of the magnetic rotation was not satisfactory, as the solution was not sensitive and very difficult to read. It gave

t.	Sp. rotation.	Mol. rotation.
71·4°	2·3615	33·708
	Phenol, 71·4°......	18·006
	Acetanilide, 71·4°..	15·702
At 15·0° corrected by temp. diff. of formanilide		0·301
	Acetanilide, 15° =	16·003

182. *Phenylacetamide*, $C_8H_9NO = C_6H_5·CH_2·CO·NH_2$.

This was prepared from phenylacetic chloride and aqueous ammonia, and then crystallised first from water distilled under reduced pressure, and finally from alcohol. It boiled at 262° (corr.) under a pressure of 250 mm., but with slight decomposition. The only suitable solvent was phenol, and even this, unless hot, did not keep sufficient in solution for measurement. The solution used had the composition $C_8H_9NO + 2·5C_6H_6O$. This contained 36·48 per cent. of amide.

Relative density of the mixture :

$d\ 67·17° = 1·07508$. $d\ 77·4° = 1·07310$.

The magnetic rotations were very difficult to read, as the product became coloured, and was not sensitive.

t.	Sp. rotation.	Mol. rotation.
78·5°	2·3397	44·826
	$2·5C_6H_6O$ at 78·5°	29·957
		14·869
For 63·5° (corrected by temp. diff. of formanilide)		0·339
	Phenylacetamide, 15·0°..	15·208

Hydrochlorides of Bases.

With the exception of dimethylaniline hydrochloride, all were examined in solution, some of them as neutral salts, others containing an excess of hydrochloric acid.

In most cases, the solutions of the neutral salts become coloured if kept even for a short time, but if free acid be present, this does not take place to the same extent, and it was for this reason that it was sometimes used.

183. *Aniline Hydrochloride.*

This salt was examined in aqueous solution, prepared by adding the theoretical quantity of hydrochloric acid and water to a weighed quantity of aniline. The solution used contained 42·53 per cent. of hydrochloride, and was very nearly saturated. The composition was $C_6H_7N,HCl + 9·722H_2O$.

Relative density of the solution:

d 15° = 1·0877. d 20° = 1·0861.

Magnetic rotation, twice determined, gave

t.	Sp. rotation.	Mol. rotation.
14·2°	1·6251	25·269
	Less water	9·722
		15·547
Plus influence of solution estimated from dimethylaniline		0·847
Dry aniline hydrochloride		16·394

184. *Dimethylaniline Hydrochloride (Anhydrous).*

It is usually stated that this salt is uncrystallisable, and it was, therefore, thought that it would be of interest to examine it in the anhydrous state, because its rotation could then be compared with that of its aqueous solution, and thus the influence of water on the rotation of this salt found.

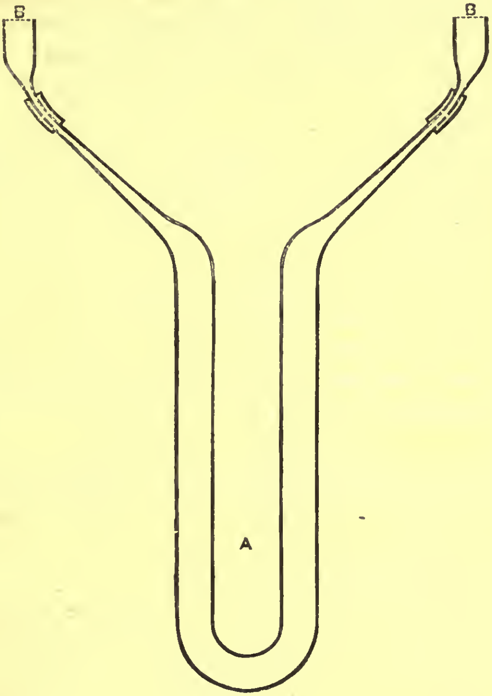
The following method was found most convenient for its preparation.

Dry hydrogen chloride was passed over a weighed quantity of colourless dimethylaniline in a small weighed flask, the temperature not being allowed to rise above that required to keep the product in a somewhat thick, oily condition; if the acid be passed through the dimethylaniline, it becomes so hot in the immediate locality of the delivery tube that it assumes a slightly greenish colour. When it was thought that the base was saturated, the flask and contents were weighed, and if it was found that enough gas had not been passed, the operation was continued a little longer, the product being warmed to render it fluid, but if too much had been absorbed, the requisite quantity of base was added to correct this, and well mixed by warming the product. In this manner the salt can be obtained nearly pure, its composition being finally determined by analysis. If a little excess of gas be allowed to remain in the salt, this can be allowed for in the calculation of the rotations.

Dimethylaniline, prepared in this way, is a transparent, pale yellow substance, becoming nearly hard on cooling. After a time, however, it solidifies to a *beautifully crystalline* mass. It is very deliquescent.

The determination of the density of this anhydrous hydrochloride presented some difficulty on account of its being nearly solid when cold, and before it crystallised. The following method, however, was successful, and it is given here as it may be useful to others.

Fig. 21.



A U-shaped density tube, represented in Fig. 21, and holding about 8·5 c.c., was employed; it was weighed, and its capacity determined very carefully by filling it perfectly with water at a known temperature, and again weighing it. The hydrochloride was then melted and drawn into the tube until it was quite full. Two small funnel-shaped tubes, previously filled with the hydrochloride, were then attached to the capillary ends of this density tube so that as contraction took place during cooling, fresh quantities of the product would be drawn in. (When putting on these funnel-shaped tubes, care should be taken to avoid air bubbles, and the hydrochloride ought to be exuding from the ends of the connectors; if contraction has already occurred in the density tube, it should be warmed until it begins to overflow before these little tubes are attached.) The apparatus is then carefully wiped or cleansed from any hydrochloride that may be on it, and suspended in a beaker and allowed to cool in a room two or three degrees *warmer* than the balance room, a delicate thermometer being placed close against it. After standing until the thermometer indicates a constant temperature, which is then noted, the funnel-shaped ends are rapidly removed, and any excess of the hydrochloride on the ends of the capillary quickly wiped off, and the beaker containing the density tube at once removed to the cooler balance room, where slight contraction will take place, and the salt recede from the capillary ends. The weighing can then be made.

For temperatures of ten or twelve degrees above the atmospheric, the tube is again provided with the funnel-shaped ends full of hydrochloride, the precautions above given being observed so as to avoid air bubbles; it is then placed in water of the requisite temperature, and after being in this for some time (the change of temperature is slow owing to the viscid nature of the substance), the small tubes are removed, and any excess wiped from the capillaries. It is then removed from the water bath, carefully dried as soon as a little contraction has taken place, and, after cooling, weighed.

Two specimens were examined, one having the composition

$$C_8H_{11}N,HCl + 0{\cdot}066HCl,$$

the other being free from excess of acid. Their rotations were fairly concordant. The following is an average of their composition, densities, and rotations.

Composition, $C_8H_{11}NHCl + 0{\cdot}033HCl$.

Relative density: $d\ 15° = 1{\cdot}1190$. $d\ 25° = 1{\cdot}1154$.

Magnetic rotation:

t.	Sp. rotation.	Mol. rotation.
16·7°	2·3363	18·399
	Less 0·033HCl (dry) ..	0·073
Dimethylaniline hydrochloride......		18·326

Dimethylaniline Hydrochloride in Aqueous Solution.

These solutions were prepared in a similar manner to the aniline hydrochloride.

Sol. I.—This had the composition $C_8H_{11}N,HCl + 0{\cdot}069HCl + 6{\cdot}174H_2O$, and contained 58·085 per cent. of hydrochloride.

Relative density of the solution:

$d\ 15° = 1{\cdot}0789$. $d\ 20° = 1{\cdot}0772$.

Magnetic rotation twice determined:

t.	Sp. rotation.	Mol. rotation.
13·8°	1·7255	24·084
	Less excess of HCl (dil.)	0·304
		23·780
	Less water............	6·174
		17·606

Sol. II.—This had the composition $C_8H_{11}N,HCl + 0·069HCl + 21·238H_2O$, and contained 29·04 per cent. of hydrochloride.

Relative density of the solution:

$d\ 15° = 1·0395$. $d\ 20° = 1·0385$.

t.	Sp. rotation.	Mol. rotation.
14·8°	1·3419	38·893
	Less excess of HCl....	0·304
		38·589
	Less water	21·238
		17·351

The following are the results from these three determinations. 100 per cent. = 18·326; 58·085 per cent. = 17·606; 29·04 per cent. = 17·351.

If they are plotted out it is found that they form a slightly curved line, the curvature diminishing as the dilution increases.

185. *Hydrochlorides of Para- and Ortho-dimethyltoluidines.*

These solutions were prepared in exactly the same proportions, an excess of acid being used. They had the composition $C_9H_{13}N,HCl + 0·5HCl + 4·17H_2O$, and contained 69·5 per cent. of $C_9H_{13}N,HCl$.

Para-salt.

Relative density of the solution:

$d\ 15° = 1·0889$. $d\ 25° = 1·0859$.

Magnetic rotation twice determined:

t.	Sp. rotation.	Mol. rotation.
18°	1·8371	24·841
	Less excess of HCl (dil.)	2·206
		22·635
	Less water	4·170
		18·465

Ortho-derivative.

Relative density of the solution:

d 15° = 1·1085. d 25° = 1·1054.

Magnetic rotation twice determined:

t.	Sp. rotation.	Mol. rotation.
17°	1·8888	25·081
	Less excess of HCl (dil.) ..	2·204
		22·877
	Less water................	4·170
		18·707

The difference of rotation of these salts is 0·240.

186. *Hydrochlorides of Phenylenediamines.*

The composition of these salts, obtained from Kahlbaum, was determined by gravimetric chlorine determinations, and gave

	Found.	Calculated.
Hydrochloride of ortho-phenylenediamine..	40·304	40·33
,, para-phenylenediamine ..	40·22	40·33
,, meta-phenylenediamine ..	40·26	40·33

They were examined in aqueous solution, but owing to the readiness with which they became coloured by oxidation if prepared under ordinary conditions, it was found impossible to get sufficient light to pass through them to determine their rotations; on this account it was necessary to make the solutions, filter them, and fill the measuring tubes in an atmosphere of carbonic anhydride. This was done by conducting all the operations in a rather deep metal vessel, open at the top, and filled with this gas, and in this manner solutions could be obtained, which were only a little coloured, but it was necessary to measure them directly they were made. It was found by direct experiment that the small amount of carbonic anhydride dissolved in these solutions had no perceptible influence on the rotation.

The meta-salt dissolves most freely in water; from a rough determination it was found that about a 30 per cent. solution was the strongest that could be made at ordinary temperature. In the case of the ortho-compound, about a 23 per cent. solution could be formed, but with the para- only a 17 per cent.

It was found best to employ solutions not quite so strong as the above, so that they might be rapidly prepared.

Ortho-salt.—This solution had the composition of $C_6H_8N_2,2HCl + 45$ mol. H_2O, and contained 18·264 per cent. of salt.

Relative density of the solution:

d 15° = 1·0646.   25° = 1·0630.

Magnetic rotation three times determined:

t.	Sp. rotation.	Mol. rotation.
15°	1·2826	66·329
	Less water	45·000
		21·329

Para-salt.—This solution had the composition $C_6H_8N_2,2HCl + 65H_2O$, and contained 13·397 per cent. of salt.

Relative density of the solution:

d 15° = 1·0454.   *d* = 25° = 1·0447.

Magnetic rotation three times determined:

t.	Sp. rotation.	Mol. rotation.
15°	1·1869	85·213
	Less water	65·000
		20·213

Meta-salt.—This solution had the composition $C_6H_8N_2,2HCl + 40H_2O$, and contained 20·08 per cent. of salt.

Relative density of the solution:

d 15° = 1·0687.   *d* 25° = 1·0672.

Magnetic rotation three times determined:

t.	Sp. rotation.	Mol. rotation.
15°	1·2884	60·345
	Less water	40·000
		20·345

Mol. rotation of ortho-salt....	21·329	−1·116
,, para-salt	20·213	+0·132
,, meta-salt....	20·345	

As the rotations of para-compounds are usually a trifle higher than those of the corresponding meta-derivatives, it may be that the para-rotation is a little low. This would not be surprising, as the solution examined contained only 13·397 per cent., and the molecular weight of these hydrochlorides is high, so that in this case a small error would have a considerable influence. Its rotation may also be a little lower from dilution.

UNSATURATED COMPOUNDS.

187. *Cinnamene*, $C_8H_8 = C_6H_5{\cdot}CH{:}CH_2$.

The process described by Fittig and Binder (*Annalen*, 1879, **195**, 137) for the preparation of this hydrocarbon was employed, namely, the decomposition of hydrobromocinnamic acid with an alkali. As cinnamene polymerises so easily when heated, it was purified by steam distillation, and then dried over potassium carbonate. Several preparations were made, and they all had practically the same density; they were kept in the dark, and examined within two or three days of their preparation.

Relative density:

d 4° = 0·9329.	*d* 10° = 0·9274.	*d* 20° = 0·9201.
d 5 = 0·9319.	*d* 15 = 0·9234.	*d* 25 = 0·9167.

188. *Allylbenzene*, $C_9H_{10} = C_6H_5{\cdot}CH{:}CH{\cdot}CH_3$.

This was prepared in an analogous manner to cinnamene, but it may be useful to add that it is necessary to employ the hydrobromic acid in as concentrated a solution as possible, otherwise the phenylcrotonic acid is only partially changed into hydrobromophenylcrotonic acid, and the yield of hydrocarbon obtained when it is treated with alkali is unsatisfactory. The allylbenzene was steam distilled, and dried with potassium carbonate before examination; when dry, it boiled at 176—177° (corr.). The boiling point previously given for this hydrocarbon, namely, 174—175° (*Chem. Soc. J.*, 1877, 381), was uncorrected.

Relative density:

d 4° = 0·9230.	*d* 10° = 0·9181.	*d* 20° = 0·9109.
d 5 = 0·9222.	*d* 15 = 0·9143.	*d* 25 = 0·9076.

189. *Isobutenylbenzene*, $C_{10}H_{12} = C_6H_5{\cdot}CH{:}C(CH_3)_2$.

This was prepared by the process described by me some years ago (*Chem. Soc. J.*, 1879, **35**, 138), namely, by heating together benzaldehyde, isobutyric anhydride, and sodium isobutyrate. When distilled from sodium, it boiled at 187·3—188·3° (corr.). The boiling point previously given for this hydrocarbon (184—186°) was uncorrected.

Relative density:

d 4° = 0·9163.	*d* 10° = 0·9116.	*d* 20° = 0·9047.
d 5 = 0·9154.	*d* 15 = 0·9081.	*d* 25 = 0·9014.

190. *Stilbene*, $C_{14}H_{12} = C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5$.

As this substance in the pure state melts at a temperature too high for its examination (124°), it was necessary to employ it in solution, using a solvent having a somewhat similar specific rotation; this was difficult to find, as stilbene is not readily soluble in ordinary solvents. The one selected was diphenylmethane; a mixture of the composition $C_{14}H_{12} + 3C_{13}H_{12}$, and containing 26·315 per cent. of stilbene, being used. To keep this in the liquid state, however, it was necessary to heat it to a temperature near to 70°.

Relative density of the mixture:

$$d\ 70° = 0{\cdot}9982. \qquad d\ 80° = 0{\cdot}9963.$$

Magnetic rotation three times determined:

t.	Sp. rotation.	Mol. rotation.
69·6°	2·7113	103·163
Less $C_{13}H_{12}$ × 3 at 69·6° = 23·499 × 3..		70·497
	Stilbene at 69·6° ..	32·666
	Estimated temp. diff. for 54·6 ..	0·477
	Stilbene at 15·0 ..	33·143

As the specific rotation of stilbene is somewhat higher than that of diphenylmethane, the latter will probably have pulled it down slightly, making this number a trifle low.

The temperature difference of unsaturated compounds is larger than that of saturated compounds; thus, taking two comparable compounds: ethylic hydrocinnamate gave 0·436, and ethylic cinnamate 0·607. If the ratio be applied to diphenylmethane, the nearest compound to stilbene for which a temperature difference has been determined, it will give for stilbene 0·874 for 100°. This is the estimate employed above.

191. *Phenyl Allyl Oxide*, $C_9H_{10}O = C_6H_5{\cdot}O{\cdot}C_3H_5$.

This was prepared from phenol by acting on it with sodium ethoxide dissolved in alcohol, and allylic iodide, the mixture being heated in the water bath for four or five hours. The crude product was washed with dilute potash and dried; when distilled, it mostly came over between 190° and 200°, some product of high boiling point being left. The distillate was slightly coloured with iodine, but this was removed by boiling it with a very small quantity of potash; it was then fractionated several times when most of it was obtained boiling between 191·5° and 192·0°. It is a colourless oil having an alliaceous odour. When boiled with sodium, the metal gradually dissolves and forms a pasty mass.

Relative density:
d 10° = 0·9890. *d* 45° = 0·9663. *d* 80° = 0·9510.
d 15 = 0·9856. *d* 50 = 0·9638. *d* 85 = 0·9493.
d 20 = 0·9813. *d* 55 = 0·9614. *d* 90 = 0·9476.
d 25 = 0·9777. *d* 60 = 0·9590. *d* 95 = 0·9460.
d 30 = 0 9744. *d* 65 = 0·9568. *d* 100 = 0·9446.
d 35 = 0·9716. *d* 70 = 0·9548.
d 40 = 0 9689. *d* 75 = 0·9528.

192. *Paratolyl Allyl Oxide*, $C_{10}H_{12}O = CH_3\cdot C_6H_4\cdot O\cdot C_3H_5$.

This was prepared from paracresol, sodium ethoxide dissolved in alcohol, and allylic iodide. Its boiling point is 212·5—216·5°.

Relative density:
d 4° = 0·9817. *d* 10° = 0·9768. *d* 20° = 0·9693.
d 5 = 0·9809. *d* 15 = 0·9728. *d* 25 = 0·9662.

193. *Anethole*, $C_{10}H_{12}O = C_3H_5\cdot C_6H_4\cdot O\cdot CH_3$.

Oil of anise was well cooled, and the crystallised anethole separated and strongly pressed between calico; it was then crystallised, once from 75 per cent., and then twice from 90 per cent. alcohol. The product was beautifully white, but had a slightly violet or blue fluorescence; it was twice fractionated, and the portion boiling between 235·2° and 235·5° collected separately (the residue did not all come over under 290°). As this appeared to contain a trace of oil it was further purified by crystallisation from alcohol.

Relative density:
d 15° = 0·9936. *d* 20° = 0·9905. *d* 25° = 0 9875.

194. *Allylic Benzoate*, $C_{10}H_{10}O_2 = C_7H_5O_2\cdot C_3H_5$.

This was produced by the action of benzoic chloride on allylic alcohol. The reaction does not set in in the cold, but on heating in the water bath hydrogen chloride is evolved from the mixture in abundance; to complete the reaction, however, a higher temperature may be afterwards employed. The product mixed with ether was washed with water and sodium carbonate solution, dried, and distilled; it came over between 229° and 234°, leaving about 25 per cent. of higher and, apparently, polymerised product, which became very thick on cooling. On redistilling the first portion, the allylic benzoate was obtained boiling at 229—230·5° (corr.). As it contained a small amount of chlorine it was heated with zinc dust and refractionated; it then boiled constantly at 230° (corr.), and was almost entirely free from chlorine.

Relative density:
d 4° = 1·0671.   d 10° = 1·0617.   d 20° = 1·0541.
d 5 = 1·0661.   d 15 = 1·0578.   d 25 = 1·0511.

195. *Isoeugenol*, $C_{10}H_{12}O_2 = CH_3\cdot CH{:}CH\cdot C_6H_3(OH)\cdot O\cdot CH_3$.

For the specimen examined, I am indebted to Professor Tiemann. It boiled at 193—194° under a pressure of 100 mm. A portion, distilled under a pressure of 760 mm., boiled at 266·5—268·5° (corr.), about one-eighth of the product polymerising. This is about 14° higher than ordinary eugenol (253—254°, corr.). The specimen of isoeugenol examined solidified when cooled with ice and salt, but it did not have a well defined, solidifying point, becoming liquid at from 9·5° to 14°.

Relative density:
d 4° = 1·0994.   d 10° = 1·0944.   d 20° = 1·0872.
d 5 = 1·0985.   d 15 = 1·0907.   d 25 = 1·0839.

196. *Eugenol*, $C_{10}H_{12}O_2 = CH_2{:}CH\cdot CH_2\cdot C_6H_3(OH)\cdot O\cdot CH_3$.

When the specimen, obtained from Kahlbaum, was fractionated, the first portions came over with a little water, but the temperature soon rose to 254°, at which most of it distilled, leaving a residue of high boiling point, apparently a polymerised body. On re-distillation it was obtained as a colourless oil boiling at 253—254° (corr.).

Relative density:
d 4° = 1·0785.   d 10° = 1·0734.   d 20° = 1·0663.
d 5 = 1·0776.   d 15 = 1·0696.   d 25 = 1·0633.

197. *Cinnamaldehyde*, $C_9H_8O = C_6H_5\cdot CH{:}CH\cdot COH$.

This was separated from oil of cassia by treating with hydrogen potassium sulphite, strongly pressing the crystalline compound between calico, washing it well with alcohol, again pressing and drying. The product was then decomposed with dilute sulphuric acid, the mixture being gently heated, and the cinnamaldehyde taken up with ether. The ethereal solution was then washed with a little dilute potash, dried with calcium chloride, and distilled. It boiled at 209·5—211·5° (corr.) under a pressure of 250 mm., most of it coming over at 209·5°. It was a colourless oil, and yielded ordinary cinnamic acid when oxidised by exposure to the air.

Relative density:
d 4° = 1·1202.   d 10° = 1·1159.   d 20° = 1·1102.
d 5 = 1·1194.   d 15 = 1·1129.   d 25 = 1·1076.

198. *Ethylic Cinnamate*, $C_{11}H_{12}O_2 = C_6H_5\cdot CH{:}CH\cdot COO\cdot C_2H_5$.

Obtained from the Badische Anilin und Soda Fabrik. This was purified by freezing and pressing very strongly between calico. It distilled at 195·5° under a pressure of 103 mm., and had a relative density *d* 15° = 1·0546. This substance at times becomes opalescent on keeping, apparently owing to polymerisation.

A second specimen of ethylic cinnamate was prepared from cinnamic acid, and purified by crystallisation by cold and pressing out any impurities between calico. This boiled at 226° (corr.) under a pressure of 250 mm., and had a relative density of 1·0556 at 15° before distillation, and 1·0552 after distillation. This is slightly higher than the above. The following are the density determinations made with the first specimen.

Relative density:

d 10° = 1·0584.
d 15 = 1·0546.
d 20 = 1·0512.
d 25 = 1·0480.
d 45 = 1·0387.
d 50 = 1·0368.
d 55° = 1·0349.
d 60 = 1·0329.
d 65 = 1·0311.
d 70 = 1·0294.
d 75 = 1·0279.
d 80 = 1·0266.
d 85° = 1·0253.
d 90 = 1·0243.
d 95 = 1·0235.
d 100 = 1·0230.

199. *α-Methylic Orthomethoxyphenylacrylate.*

Prepared from coumarin (Trans., 1877, **31**, 418). This boiled at 246·5—247·5° (corr.) under a pressure of 250 mm., and at 301—302° under a pressure of 760 mm.

Relative density:

d 4° = 1·1494.
d 5 = 1·1485.
d 10° = 1·1444.
d 15 = 1·1406.
d 20° = 1·1372.
d 25 = 1·1343.

200. *β-Methylic Orthomethoxyphenylacrylate.*

This was prepared by boiling the α-ether with a very small quantity of iodine. When saponified, it was found to yield the β-acid with only a trace of the α-acid. It boiled at 304—305° (corr.).

Relative density:

d 4° = 1·1522.
d 5 = 1·1513.
d 10° = 1·1472.
d 15 = 1·1432.
d 20° = 1·1395.
d 25 = 1·1371.

201. *Cinnamic Alcohol*, $C_9H_{10}O = C_6H_5\cdot CH{:}CH\cdot CH_2\cdot OH$.

The crystallised cinnamic alcohol, obtained from Kahlbaum, was kept pressed between porous plates until free from the small quantity of oily product it contained. It was then distilled, and came over at 257·5° (corr.), leaving a small quantity of a substance of higher boiling point in the retort. On a second distillation, it had the same boiling point, and was obtained as a colourless oil, which soon solidified to a hard crystalline mass.

Relative density:

d 35° = 1·0397.
d 40 = 1·0380.
d 45 = 1·0364.
d 50 = 1·0348.
d 55 = 1·0333.
d 60° = 1·0318.
d 65 = 1·0305.
d 70 = 1·0294.
d 75 = 1·0283.
d 80 = 1·0273.
d 85° = 1·0266.
d 90 = 1·0261.
d 95 = 1·0259.
d 100 = 1·0258.

202. *Benzylidene-acetone*, $C_{10}H_{10}O = C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3$.

Relative density:

d 15° = 1·0377.
d 20 = 1·0347.
d 25 = 1·0320.
d 30 = 1·0295.
d 35 = 1·0272.
d 40 = 1·0251.
d 45° = 1·0232.
d 50 = 1·0213.
d 55 = 1·0196.
d 60 = 1·0179.
d 65 = 1·0163.
d 70 = 1·0148.
d 75° = 1·0135.
d 80 = 1·0122.
d 85 = 1·0113.
d 90 = 1·0106.
d 95 = 1·0103.
d 100 = 1·0102.

REFRACTION DETERMINATIONS.

For the measurements of the substances marked (G) I am indebted to Dr. Gladstone, they were made with the same specimens as those used for the magnetic rotations.

	T.	μA.	μD.	μF.	μH.	$\frac{\mu A - 1}{d}p.$	$R_H—R_A$.
Benzene, from benzoic acid (G)	18·5	1·4927	1·5027	—	1·5357	43·59	—
Metaxylene (G)	22·5	1·4876	—	1·5079	1·5277	59·960	4·92
Paraxylene (G)......	23·7	1·4854	—	1·5058	1·5253	59·981	4·93
Orthoxylene (G).....	24·1	1·4928	—	1·5129	1·5328	59·801	4·85
Isobutenylbenzene (G)	21·0	1·5269	1·5390	—	1·5834	77·200	—

Hydrindene.

I. Hydrindene (from coal tar). Distilled three times from sodium, from Kramer and Spilker: density, *d* 10·6°/4° = 0·95980. II. Hydrindene (synthetically prepared): density, 16·4°/4° = 0·96250.

		μ 10·6°.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d}p.$	Dispersion $H_\gamma—H_\alpha$.
Hydrindene I,	A	1·52908	0·55123	65·046	—
,,	H_α	1·53431	0·55669	65·689	3·348
,,	D	1·53896	0·56153	66·261	—
,,	H_β	1·55105	0·57412	67·747	—
,,	H_γ	1·56154	0·58506	69·037	—

	μ 16·4°.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d} p$.	Dispersion H_{γ}—H_{α}.
Hydrindene II, A	1·52889	0·54950	64·850	—
,, H_{α}	1·53394	0·55474	65·460	3·369
,, D	1·53877	0·55977	66·053	—
,, H_{β}	1·55114	0·57261	67·578	—
,, H_{γ}	1·56136	0·58323	68·829	—

Indene.

I. From coal-tar; distilled from sodium three times, from Krämer and Spilker: density, *d* 12·7°/4° = 1·01995. II. Synthetically prepared: density, *d* 8·2°/4° = 1·00227.

	μ 12·7°.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d} p$.	Dispersion H_{γ}—H_{α}.
Indene I, A	1·55818	0·54726	63·482	—
,, H_{α}	1·56454	0·55349	64·205	4·284
,, D	1·57107	0·55990	64·948	—
,, H_{β}	1·58743	0·57594	66·809	—
,, H_{γ}	1·60220	0·59042	68·489	—
	μ 8·2°.			
Indene II, A	1·56680	0·56551	65·599	—
,, H_{α}	1·57354	0·57224	66·380	4·473
,, D	1·57980	0·57849	67·104	—
,, H_{β}	1·59693	0·59557	69·086	—
,, H_{γ}	1·61219	0·61080	70·853	—

Diphenylmethane, Triphenylmethane, and Diphenyl.

These three hydrocarbons were examined at the same temperature so that the numbers might be comparable, and as triphenylmethane melts at 92°, it was necessary that it should be above this. The temperature used was 99°. Diphenylmethane: density, *d* 99°/4° = 0·94402. Triphenylmethane: density, *d* 99°/4° = 1·01405. Diphenyl: density, *d* 99°/4° = 0·97165.

	μ 99·0°.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d} p$.	Dispersion H_{γ}—H_{α}.
Diphenylmethane, H_{α}......	1·53474	0·56644	95·162	—
,, H_{β}......	1·55390	0·58674	98·572	5·691
,, H_{γ}......	1·56615	0·59972	100·753	—
Triphenylmethane, H_{α}	1·57776	0·56975	139·019	—
,, H_{β}......	1·59965	0·59134	144·286	8·632
,, H_{γ}	1·61364	0·60513	147·651	—
Diphenyl, H_{α}......	1·56841	0·58499	90·088	—
,, H_{β}......	1·59441	0·61175	94·209	6·843
,, H_{γ}......	1·61158	0·62942	96·931	—

Oxides.

	T.	μA.	μF.	μH.	$\frac{\mu A-1}{d}p.$	R_H-R_A.
Methyl paratolyl oxide (G) ..	8·9	1·5092	1·5314	1·5535	63·37	5·51
Methyl metatolyl oxide (G) ..	13·5	1·5074	1·5293	1·5513	63·31	5·48
Methyl orthotolyl oxide (G) .	15·4	1·5107	1·5329	1·5549	63·25	5·47
Dimethylresorcinol (G)	10·9	1·5149	1·5367	—	66·73	—
Methylguaiacol. Veratrole (G)	10·9	1·5268	1·5503	1·5741	66·68	5·98

α-Naphthyl Ethyl Oxide.

Density, 32·3°/4° = 1·04910. 32·8°/4° = 1·04883.

	t.	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p.$	Dispersion $H_\gamma-H_\alpha$.
A	32·8°	1·57922	0·55225	94·987	—
H_α ...	32·3	1·58787	0·56036	96·382	7·922
D	32·8	1·59509	0·56738	97·590	—
H_β ...	32·3	1·61645	0·58760	101·067	—
H_γ ...	32·3	1·63619	0·60642	104·304	—

β-Naphthyl Ethyl Oxide.

Density, 35·6°/4° = 1·05013. 36°/4° = 1·04988.

	t.	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p.$	Dispersion $H_\gamma-H_\alpha$.
A	35·6°	1·58191	0·55413	95·311	—
H_α ...	36·0	1·59012	0·56208	96·678	7·779
D	35·6	1·59752	0·56899	97·867	—
H_β ...	36·0	1·61834	0·58896	101·301	—
H_γ ...	36·0	1·63760	0·60731	104·457	—

Ethereal Salts.

	T.	μA.	μF.	μH.	$\frac{\mu A-1}{d}p.$	R_H-R_A.
Ethylic anisate (G)........	9·0	1·5187	1·5438	1·5707	83·79	8·40
Ethylic methylsalicylate (G)	16·2	1·5145	1·5374	1·5620	83·04	7·67

Ethylic α- and β-Naphthoates.

These two compounds were examined at temperatures above the fusing point of the β-salt, for the purposes of comparison. Ethylic α-naphthoate: density, *d* 57·5°/4° = 1·09194. Ethylic β-naphthoate: density, *d* 57°/4° = 1·08582.

	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p.$
Ethylic α-naphthoate, H_α	1·56894	0·52103	104·206
" " D	1·57643	0·52789	105·578
" " H_β	1·59664	0·54640	109·280
" " H_γ	1·61573	0·56388	112·776

	μ.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d}p$.
Ethylic β-naphthoate, H_α	1·57316	0·52790	105·580
,, ,, D	1·58069	0·53479	106·958
,, ,, H_β	1·60142	0·55388	110·776

Phenylazoimide.

The following is the average of two sets of measurements: density, 10·8°/4° = 1·09672.

	μ 10·8°.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d}p$.	Dispersion H_β—A.
A	1·54764	0·49934	59·421	—
H_α	1·55457	0·50566	60·173	3·350
D	1·56104	0·51156	60·875	—
H_β	1·57851	0·52749	62·771	—

Bases.

	μA.	μF.	μH.	$\frac{\mu_A - 1}{d}p$.	R_H—R_A.
Dimethylaniline (G), *t.* 8·2°	1·5514	1·5834	1·6198	68·96	8·55

These agree very closely with my results (Trans., 1892, **61**, 302).

	μA.	μF.	μH.	$\frac{\mu_A - 1}{d}p$.	R_H—R_A.
Methyldiphenylamine (G), *t.* 24·6°	1·5998	1·6391	1·6774	104·88	13·56
Benzylaniline (G), *t.* 26·3°	1·5967	1·6297	1·6660	102·93	11·95

The measurements of aniline and of α-naphthylamine will be found in this Journal (Trans., 1892, **61**, 301 and 303), and also those of ortho- and para-toluidine (Trans., 1896, **69**, 4).

Metaphenylenediamine.

The following numbers are the average of two closely concordant sets of measurements, that for the Li line, however, is a single result. Density, 57·7°/4° = 1·10696.

Line.	*t.*	μ.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d}p$.	Dispersion H_γ—H_α.
A	57·7°	1·61690	0·55729	60·187	—
Li	56·5	1·62449	0·56369	60·878	—
H_α	57·7	1·62558	0·56513	61·034	4·935
D	57·7	1·63390	0·57264	61·845	—
H_β	57·7	1·65600	0·59261	64·001	—
H_γ	57·7	1·67617	0·60183	65·969	—

Dimethylortho- and Dimethylpara-toluidines.

The following are calculated for Gladstone's formula from Brühl's results. (*Zeit. physikal. Chem.*, 1895, **16**, 2, 224.) Dimethylorthotoluidine: density, *d* 23·3°/4° = 0·9250. Dimethylparatoluidine: density, *d* 20·2°/4° = 0·9366.

		μ 23·3°.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d}p$.	Dispersion H_γ—H_α.
Dimethylorthotoluidine,	H_α.	1·51932	0·56142	75·972	4·245
,,	H_γ.	1·54841	0·59287	80·037	
		μ 20·2°.			
Dimethylparatoluidine,	H_α.	1·54061	0·57720	77·922	5·366
,,	H_γ.	1·57784	0·61695	83·288	

β-Naphthylamine.

As in the case of the magnetic rotation of this substance, it was fused with its own weight of α-naphthylamine for examination. Two sets of measurements were made and gave very concordant results.

Density, *d* 98°/4° = 1·0614.

Line.	μ 98°.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d}p$.
A	1·62746	0·59116	169·072
H_α..........	1·63886	0·60190	172·143
D	1·64927	0·61207	175·286
H_β..........	1·67960	0·64028	183·120
H_γ..........	1·70193	0·66132	189·137

On subtracting the molecular refraction of α-naphthylamine at 98° from these numbers that of the β-compound will be obtained, thus:

Line.	Mixture.	α-Naphthylamine.	β-Naphthylamine.	Diff.
A	169·072	84·018	85·054	1·036
H_α	172·143	85·473	86·670	1·197
D	174·949	86·890	88·059	1·169
H_β	183·120	90·928	92·192	1·264

Dispersion, H_β—A = 7·138.

This is rather higher than that of α-naphthylamine at 98°, which for the same lines gives 6·910.

Dimethyl-α-Naphthylamine.

This substance being liquid under ordinary circumstances, was first examined at the temperature of the atmosphere, and then at about the same temperature as that used for the β-compound. The measurement of the line A was made twice for each temperature and on different occasions. That of the lithium line was also made twice for the lower, but only once at the higher temperature, whilst for all the other lines three different sets of measurements were made. The numbers agreed very closely amongst themselves. The following are the averages of the results. Densities, *d* 10·1°/4°, 1·04755; *d* 10·8°/4°, 1 04694; *d* 11·8°/4°, 1·04623.

	Line.	*t*.	*μ*.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d} p$.	Disp. H_γ—H_α.
I.	A	10·1°	1·60916	0·58151	99·438	—
	Li	11·8	1·61594	0·58872	100·671	—
	H_α	10·8	1·61787	0·59016	100·917	9·544
	D	11·8	1·62609	0·59842	102·329	—
	H_β	10·8	1·65158	0·62237	106·425	—
	H_γ	10·8	1·67629	0·64597	110·461	—
II.	A	50·9	1·58951	0·58009	99·188	—
	Li	54·7	1·59509	0·58737	100·440	—
	H_α	51·6	1·59780	0·58854	100·640	9·528
	D	51·6	1·60659	0·59719	102·119	—
	H_β	51·6	1·63059	0·62082	106·160	—
	H_γ	51·6	1·65440	0·64426	110·168	—

Temperature Differences.

	I.	II.	Temp. diff. for 40·8°.	Temp. diff for 100°.
A	99·438	99·188	0·250	0 612
Li......	100·671	100·440	0·231*	0·532
H_α	100·917	100·641	0·276	0·676
D	102·329	102·119	0·210	0·527
H_β	106·425	106·160	0·265	0·649
H_γ	110·461	110·168	0·293	0·718
			Average	0·619

From these numbers it will be found that the dispersion of dimethyl-α-naphthylamine is about the same as that of α-naphthylamine, the latter giving for H_β—A 7·010 (Trans., 1892, **61**, 303), whilst the above gives for the same comparison 6·987. The temperature differences, however, are larger, averaging 0·619 for 100°, whereas those of α-naphthylamine average only 0·461.

Dimethyl-β-Naphthylamine.

The following results are averages of three sets of closely concordant measurements, for all except the A and lithium lines.

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* In these cases the differences were 43° and 39·8° respectively.

These were only measured on one occasion. The H_γ was rather difficult to read.

Line.	t.	μ.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d}p$.
A	56·3°	1·62007	0·60429	103·333
Li	56·3	1·62964	0·61361	104·927
H_α	53·2	1·63291	0·61545	105·241
D	53·2	1·64432	0·62650	107·131
H_β	53·2	1·67682	0·65810	112·535
H_γ	53·2	1·71289	0·69318	118·533

The dispersion is enormous, being for H_γ—H_α 13·292, or for H_β—A 9·202; this is much greater than that of α-naphthylamine, which is only 7·010 for the latter lines.

Hydrochlorides.

I. *Surfused Anhydrous Hydrochloride of Dimethylaniline.*

Average of two sets of measurements. Density, 18·5°/4° = 1·1156.

Line.	μ 18·5°.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d}p$.	Dispersion H_γ—H_α.
A	1·55636	0·49870	78·545	—
H_α	1·56140	0·50322	79·257	—
D	1·56619	0·50752	79·934	3·910
H_β	1·57829	0·51837	81·643	—
H_γ	1·58910	0·52805	83·167	—

II. *Solution of Hydrochloride of Dimethylaniline.*

Composition $C_8H_{11}N,HCl + 6{\cdot}174OH_2$.

With this, the following results were obtained for $\frac{\mu - 1}{d}p$.

H_α.	H_β.	H_γ.	Dispersion of salt in solution H_γ—H_α.
77·688	80·222	81·980	4·292

Aniline Hydrochloride.

This could be only examined in solution. That used had the composition $C_6H_7N,HCl + 9{\cdot}722OH_2$. It gave for $\frac{\mu - 1}{d}p$:

H_α.	D.	H_β	H_γ.	Dispersion H_γ—H_α.
63·457	63·932	65·700	66·141	2·684

TABLES OF THE SPECIFIC AND MOLECULAR ROTATIONS AND TEMPERATURE DIFFERENCES OF SUBSTANCES MENTIONED IN THIS PAPER.

The following tables contain the molecular rotations and temperature differences of all the compounds mentioned, and also most of the specific rotations, but in cases where the substance examined was dissolved in a solvent, the specific rotation actually determined being that of the solution, the result is not given; in place of it, there is a reference to the page where the specific rotation in question will be found, as well as the details of the calculations by which the molecular rotation was estimated.

Many of the rotations at low temperatures incorporated in these tables have been already published.

FATTY COMPOUNDS.

	T.	Specific rotation.	Molecular rotation.	Temperature difference for 100° on mol. rot.
1. Heptane	15·0°	0·9500	7·666	
,, ...	86·2	0·8674 [3]*	7·461	0·288 or 3·763 p. c.
2. Acetic acid	21·0	0·7976	2·525	
,, ,, ...	86 0	0·7527 [2]	2·493	
,, ,, corrected to.....	15·0	0·8016	2·528	0·049 or 1·947 p. c.
3. Propionic acid.............	20·3	0·8369	3·462	
,, ,, ...	91·0	0·7928 [2]	3·438	
,, ,, corrected to	15·0	0·8412	3·464	0·034 or 0·981 p. c.
4. Œnanthylic acid	14·5	0·9652	7·554	
,, ,, ...	91·4	0·9192 [3]	7·465	
,, ,, corrected to	15·0	0·9649	7·554	0·113 or 1·497 p. c.
5. Ethylic œnanthate.........	15·0	0·9480	9·542	
,, ,, ...	92·1	0·8917 [2]	9·413	0·167 or 1·748 p. c.
6. Chloracetic acid†	14·4	—	3·884	
,, ,, ...	64·5	1·0302 [1]	3·868	
,, ,, corrected to	15·0	—	3·882	0·032 or 0·824 p. c.
7. Dichloracetic acid	13·5	1·1628	5·299	
,, ,, ...	90·7	1·1102 [3]	5·247	
,, ,, corrected to	15·0	1·1615	5·300	0·067 or 1·271 p. c.
8. Trichloracetic acid†	14·3	—	6·473	
,, ,, ...	60·6	1·1523 [2]	6·422	
,, ,, corrected to	15·0	—	6·473	0·110 or 1·700 p. c.
9. Dipropyl ketone...........	14·8	0·9686	7·471	
,, ...	90·0	0·9041 [2]	7·337	
,, corrected to	15 0	0·9683	7·471	0·178 or 2·387 p. c.
10. Ethylic acetoacetate	16·3	0·9278	6·501	
,, ,, ...	91·0	0·8785 [1]	6·448	
,, ,, corrected to	15·0	0·9289	6·502	0·071 or 1·093 p. c.

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* The small figures in brackets give the number of times the rotation of the compound was determined at the given temperature.

† Determined in aqueous solution.

	T.	Specific rotation.	Molecular rotation.	Temperature difference for 100° on mol. rot.
11. Dimethylacetylacetone	19·3	0·9442	7·042	
,, ...	92·3	0·9030 [1]	6·995	
,, corrected to	15·0	0·9475	7·045	0·064 or 0·909 p. c.
12. Hydracetylacetone	14·9	1·0362	5·871	
,, ...	95·1	0·9784 [1]	5·831	
,, corrected to	15·0	1·0361	5·871	0·050 or 0·852 p. c.
13. Ethylene dichloride.........	14·4	1·2569	5·481	
,, ,, ...	62·5	1·1951 [1]	5·431	
,, ,, corrected to	15·0	1·2564	5·484	0·114 or 2·078 p. c.
14. Octylic chloride	8·4	1·0879	10·155	
,, ,, ...	90·6	1·0170 [3]	9 952	
,, ,, corrected to..	15·0	1·0802	10·139	0·250 or 2·465 p. c.
15. Propylic bromide	10·7	1·3811 [3]	6·889	
,, ,, ...	65·5	1·2899 [2]	6·774	
,, ,, corrected to..	15·0	1·3733	6·880	0·210 or 3·050 p. c.
16. Octylic bromide	13·0	1·2543	12·031	
,, ,, ...	92·1	1·1814 [2]	11·803	
,, ,, corrected to..	15·0	1·2517	12·025	0·288 or 2·397 p. c.
17. Ethylic iodide.............	11·0	2·2808 [4]	10·098	
,, ,, ...	64·3	2·1333 [2]	9·888	
,, ,, corrected to ...	15·0	2·2675	10·082	0·394 or 3·905 p. c.
18. Octylic iodide	16·5	1·6259	16·175	
,, ,, ...	81·9	1·5462 [2]	15·864	
,, ,, corrected to	15·0	1·6282	16·182	0·474 or 2·929 p. c.
19. Methylene diiodide	12·2	4·1892 [3]	18·677	
,, ,, ...	55·4	4·0257 [1]	18·325	0·8194
,, ,, ...	*92·0	3·9114 [1]	17·949	0·9122
,, ,, corrected to	15·0	4·1731	18·644	†0·863 or 4·622 p. c.
20. Pyrotartaric anhydride	11·6	0·9338	4·762	
,, ,, ...	50·0	0·9088 [1]	4·727	
,, corrected to	15·0	0·9303	4·759	0·091 or 1·921 p. c.
21. Ethylic citraconate	‡16·0	1·0635	10·495	
,, ,, ...	76·0	1·0167 [1]	10·363	
,, ,, corrected to	15·0	1·0645	10·497	0·220 or 2·096 p. c.
22. Citraconic anhydride.......	17·4	1·1115 [2]	5·541	
,, ,, ...	65·7	1·0717 [1]	5·477	
,, corrected to	15·0	1·1139	5·543	0·132 or 2·390 p. c

Aromatic Ethereal Salts and Phenylic Salts of Fatty Acids.

	T.	Specific rotation.	Molecular rotation.	Temperature difference for 100° on mol. rot.
23. Methylic benzoate..........	11·5	1·8523 [1]	12·757	
,, ,, corrected to	15·0	—	12·743	
24. Ethylic benzoate............	12·9	1·7533 [2]	13·862	
,, ,, corrected to	15·0	—	13·854	
25. Propylic benzoate...........	15·4	1·6773 [4]	14·875	
,, ,, corrected to	15·0	—	14·873	
26. Isopropylic benzoate	14·2	1·6705 [4]	14·953	
,, corrected to	15·0	—	14·950	

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* These readings were difficult on account of the product becoming coloured by heating.

† Average temperature difference.

‡ Average of three specimens of ethylic citraconate prepared in different ways.

	T.	Specific rotation.	Molecular rotation.	Temperature difference for 100° on mol. rot.
27. Butylic benzoate...........	16·1	1·6295 [2]	15·948	
,, ,, corrected to	15·0	—	15·952	
28. Isobutylic benzoate........	13·5°	1·6310 [2]	16·054	
,, ,, corrected to	15·0	—	16·048	
29. Octylic benzoate...........	18·1	1·4845 [2]	19·979	
,, ,, corrected to	15·0	—	19·992	
30. Ethylic phenylacetate......	14·0	1·7222	14·986	
,, ,, corrected to	15·0	—	14·982	
31. Phenylacetic or α-toluic acid (dissolved in ethylic benzoate, $CH_2Ph\cdot COOH$ +	16·2	(p. 1175)	12·739	
$2CH_2Ph\cdot COOEt$) corrected to	15·0	—	12·735	
32. Ethylic hydrocinnamate....	15·9	1·6684 [2]	16·165	
,, ,, corrected to	15·0	1·6697	16·169	
,, ,, ...	80·9	1·5913	15·898	0·410 or 2·54 p. c.
33. Ethylic cuminate..........	21·3	1·5913 [3]	17·067	
,, ,, corrected to	15·0	—	17·093	
34. Methylic salicylate.........	15·8	2·0071 [2]	14·263	
,, ,, corrected to	15·0	—	14·266	
35. Ethylic salicylate..........	15·0	1·8934 [2]	15·362	
,, ,, corrected to	15·0	—	15·366	
36. Ethylic methylsalicylate....	18·6	1·9092 [3]	17·141	
,, ,, corrected to	15·0	—	17·156	
37. Ethylic anisate............	16·9	1·9144 [4]	17·277	
,, ,, corrected to	15·0	—	17·285	
38. Ethylic metamethoxybenzoate	18·4	1·8383 [2]	16·666	
,, ,, corrected to	15·0	—	16·679	
39. Ethylic orthotoluate.......	15·2	1·7177 [2]	15·064	
,, paratoluate........	15·0	1·6678 [2]	14·744	
40. Ethylic phthalate..........	17·6	1·5416 [2]	16·900	
,, ,, corrected to	15·0	1·5448	16·909	
,, ,, ...	73·6	1·4920 [1]	16·713	0·334 } *
,, ,, ...	83·11	1·4821 [2]	16·644	0·358 }
41. Ethylic meta- or isophthalate	19·2	1·5454 [2]	16·928	
,, ,, corrected to	15·0	—	16·942	
42. Ethylic terephthalate......	47·2	1·4390 [2]	16·006	
,, ,, ...	15·0	—	16·117	
43. Ethylic benzoylacetate.....	18·8	1·7201 [2]	16·389	
,, ,, corrected to	15·0	1·7260	16·411	
,, ,, ...	100·6	1·6249 [2]	15·908	0·59 or 3·612 p. c.
44. Ethylic α-naphthoate......	15·3	2·7552 [3]	27·158	
,, ,, corrected to	15·0	—	27·161	
,, β-naphthoate......	16·0	2·7581 [2]	27·347	
,, ,, corrected to	15·0	—	27·360	
,, ,, ...	32·2	2·7176	27·164	1·129 or 5·224 p.c.
45. Phenylic acetate...........	15·9	1·8518 [3]	12·950	
,, ,, corrected to	15·0	1·8506	12·953	
,, ,, ...	69·5	1·7755 [2]	12·783	0·311 or 2·404 p.c.
46. Phenylic propionate........	15·6	1·7287 [3]	13·671	
,, ,, corrected to	15·0	—	13·673	
47. Phenylic butyrate.........	15·7	1·6622 [3]	14·759	
,, ,, corrected to	15·0	—	14·761	

* Average temp. diff. = 0·346 for 100° or 2·048 per cent. on mol. rotation.

	T.	Specific rotation.	Molecular rotation.	Temperature difference for 100° on mol. rot.
48. Phenylic œnanthate........	13·1	1·5406 [3]	17·932	
,, ,, corrected to	15·0	1·5377	17·923	
,, ,, ...	72·18	1·4747 [1]	17·653	0·477 or 2·661 p. c.
Nitro-derivatives of Aromatic Hydrocarbons.				
49. Nitrobenzene..............	19·0	1·6515 [3]	9·356	
,, corrected to	15·0	1·6566	9·361	
,, ...	56·0	1·6149 [1]	9·310	0·1243 or 1·327 p. c.
50. Metadinitrobenzene (dissolved in nitrobenzene, $C_6H_4(NO_2)_2 + 3C_6H_5{\cdot}NO_2$)	17·1	(p. 1181)	9·649	
,, corrected to	15·0	—	9·647	
51. Orthonitrotoluene	18·0	1·6492 [2]	10·802	
,, corrected to	15·0	—	10·806	
52. Paranitrotoluene	54·3	1·5207 [2]	10·166	
,, corrected to	15·0	—	10·214	
53. α-Nitronaphthalene (dissolved in nitrobenzene, $C_{10}H_7{\cdot}NO_2 + 2C_6H_5{\cdot}NO_2$)	16·2	(p. 1181)	20·841	
,, corrected to	15·0	—	20·840	
Hydroxy-derivatives of Aromatic Hydrocarbons.				
54. Phenol..................	39·0	2·4646 [2]	12·073	
,, corrected to........	15·0	—	12·140	
,, ...	88·8	2·4030	11·957	0·233 or 1·919 p. c.
55. Phenol (in aqueous solution, $C_6H_6O + H_2O$)	15·5	(p. 1182)	12·095	
,, corrected to	15·0	—	12·096	
56. Orthocresol	16·0	2·3417 [3]	13·379	
,, corrected to....	15·0	—	13·382	
57. Paracresol...............	17·0	2·2251 [4]	12·864	
,, corrected to	15·0	—	12·869	
58. Paracresol (in aqueous solution, $C_7H_8O + H_2O$)	23·4	(p. 1182)	12·749	
,, corrected to	15·0	—	12·768	
59. Metacresol...............	17·9	2·2075 [4]	12·769	
,, corrected to	15·0	—	12·776	
60. Thymol..................	16·3	1·8916 [2]	16·116	
,, corrected to	15·0	1·8938	16·120	
,, ...	57·4	1·8398 [1]	15·974	0·348 or 2·158 p. c.
61. Carvacrol................	15·6	1·9194 [3]	16·311	
,, corrected to......	15·0	—	16·313	
62. Homopyrocatechol.........	30·9	2·2502 [2]	13·269	
,, corrected to	15·0	—	13·306	
63. Resorcinol (in aqueous solution, $C_6H_6O_2 + 3{\cdot}5H_2O$)	16·6	(p. 1184)	12·099	
,, corrected to	15·0	—	12·090	
,, (in aqueous solution $C_6H_6O_2 + 14{\cdot}066H_2O$)	15·0	(p. 1184)	11·916	
,, ,,	15·0	(p. 1184)	12·285*	

* Estimated rotation of dry substance from the two solutions of resorcinol.

	T.	Specific rotation.	Molecular rotation.	Temperature difference for 100° on mol. rot.
64. Pyrocatechol (in aqueous solution, $C_6H_6O_2$ + $24·445H_2O$)	15·0	(p. 1184)	12·628	
,, ,,	15·0	—	13·022*	
65. Pyrogallol (in aqueous solution $C_6H_6O_3$ + $15·542H_2O$, average for two specimens)	16·0	(p. 1185)	12·669	
,, ,,	16·0	—	13·029	
66. Creosol....................	17·2	2·1973 [3]	15·401	
,, corrected to	15·0	—	15·405	
67. Isocreosol..................	24·8	2·1340 [3]	15·000	
,, corrected to	15·0	—	15·021	
Mixed Oxides containing Aromatic Radicles.				
68. Phenyl methyl oxide (anisole)	21·1	2·3105 [2]	13·941	
,, ,, †corrected to	15·0	—	13·958	
69. Phenyl ethyl oxide (phenetole)	20·5	2·1542 [2]	15·114	
,, ,, corrected to	15·0	—	15·129	
70. Phenyl propyl oxide	17·9	2·0360 [3]	16·179	
,, ,, corrected to	15·0	—	16·187	
71. Phenyl isopropyl oxide.....	18·3	2·0231 [3]	16·192	
,, ,, corrected to	15·0	—	16·201	
72. Phenyl isobutyl oxide	22·2	1·9278 [2]	17·311	
,, ,, corrected to	15·0	—	17·332	
73. Phenyl octyl oxide	15·5	1·7120 [3]	21·445	
,, ,, corrected to	15·0	—	21·446	
74. Orthotolyl methyl oxide....	14·3	2·2086 [2]	15·187	
,, ,, corrected to	15·0	—	15·190	
75. Paratolyl methyl oxide.....	14·5	2·1188 [2]	14·713	
,, ,, corrected to	15·0	—	14·712	
76. Metatolyl methyl oxide.....	14·4	2·1115 [2]	14·648	
,, ,, corrected to	15·0	—	14·646	
77. Dimethylresorcinol	14·2	2·0940 [2]	15·113	
,, ,, corrected to	15·0	—	15·108	
78. Guaiacol	15·6	2·4284 [3]	14·687	
79. Orthodimethoxybenzene.... (Veratrole). I	14·8	2·3880 [2]	16·842	
,, ,, corrected to	15·0	—	16·841	
,, II‡	15·1	2·3964 [1]	16·833	
,, ,, corrected to	15·0	—	16·837	
80. Dimethylquinol	55·8	2·2563 [3]	16·438	
,, corrected to	15·0	—	16·717	
,, ...	93·0	2·1947 [1]	16·183	0·085 or 4·097 p. c.
81. Dimethylhomopyrocatechol I	16·0	2·1890 [2]	17·458	
,, II‡	15·0	2·1893 [2]	17·504	
,, average of I and II	15·5	—	17·481	
,, ,, corrected to	15·0	—	17·484	

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* Estimated rotation of dry substance, on the assumption that it differs for solution in the same manner as resorcinol.

† The temperature coefficient used for this and the following analogous compounds is 0·0029 for 1° = average of that of phenol and thymol.

‡ Another specimen.

	T.	Specific rotation.	Molecular rotation.	Temperature difference for 100° on mol. rot.
82. Trimethylpyrogallol........	48·7	2·0221 [3]	17·002	
,, corrected to	15·0	—	17·201	
,, ...	91·2	1·9618 [2]	16·739	0·6211 or 3·622 p. c.
83. α-Naphthyl ethyl oxide	14·5	3·5902 [3]	32·245	
,, ,, corrected to	15·0	3·5877	32·237	
,, ,, ...	43·4	3·4918 [2]	31·777	1·671 or 5·184 p. c.
84. β-Naphthyl ethyl oxide	41·9	3·3364 [2]	30·247	
,, ,, corrected to	15·0	—	30·698	
85. Benzyl methyl oxide.......	15·0	1·9224	13·417	
Aromatic Hydrocarbons.				
86. Benzene..................	12·8	2·3124 [3]	11·294	
,, corrected to	15·0	2·3053	11·284	
,, ...	56·0	2·1856 [1]	11·104	0·436 } *
,, ...	71·4	2·1383 [2]	10·990	0·518 }
87. Toluene†	13·1	2·0781 [4]	12·158	
,, corrected to	15·0	2·0748	12·157	
,, ...	53·7	1·9790 [1]	11·937	0·543 } ‡
,, ...	80·1	1·9249 [1]	11·811	0·518 }
88. Ethylbenzene I§	19·5	1·9770 [2]	13·369	
,, corrected to	15·0	—	13·382	
,, II†.........	15·0	1·9902 [1]	13·446	
,, ...	15·0	—	13·414‖	
89. Propylbenzene	14·8	1·8926 [3]	14·554	
,, corrected to	15·0	—	14·553	
90. Isobutylbenzene	15·0	1·8275 [3]	15·615	
91. Orthoxylene	18·6	1·9894 [3]	13·325	
,, corrected to....	15·0	—	13·345	
92. Metaxylene I¶	18·9	1·8873 [2]	12·831	
,, corrected to	15·0	—	12·853	
,, II†............	16·3	1·8957 [3]	12·859	
,, corrected to	15·0	—	12·866	
,, average of I and II	15·0	—	12·859	
93. Paraxylene	17·8	1·8781 [3]	12·797	
,, corrected to....	15·0	—	12·810	
94. Mesitylene	18·9	1·7333 [6]	13·343	
,, corrected to....	15·0	1·7412	13·366	
,, ...	78·3	1·6344 [2]	13·002	0·574 or 4·271 p. c.
95. Pseudocumene	17·5	1·8444 [5]	13·983	
,, corrected to	15·0	1·8498	13·998	
,, ...	54·1	1·7762 [1]	13·764	0·598 } **
,, ...	89·0	1·7231 [1]	13·543	0·607 }
96. Cumene (Isopropylbenzene)	15·3	1·9019	14·631	
,, ,, corrected to	15·0	—	14·633	

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* Average temp. diff. for 100° = 0·477.

† From the sulphonic acid.

‡ Average temp. diff. for 100° = 0·530.

§ Obtained from Kahlbaum.

‖ Average rotation of specimens I and II.

¶ Specimen from Langfeld and Reuter.

** Average temp. diff. = 0·602 or 4·300 p. c.

	T.	Specific rotation.	Molecular rotation.	Temperature difference for 100° on mol. rot.
97. Cymene*	15·7	1·7655 [2]	15·251	
,, corrected to	15·0	—	15·255	
98. Naphthalene	89·5	3·5096 [1]	24·791	
,, corrected to	15·0	—	25·125	0·458 or 1·760 p.c.
99. Naphthalene (solution in toluene, $C_{10}H_8 + 4C_7H_8$) .	15·8	(p. 1195)	25·129	
,, ,, corrected to	15·0	—	25·125	
100. Diphenylmethane	26·4	2·5598 [2]	23·774	
,, corrected to	15·0	2·5553	23·845	
,, ...	88·1	2·4696 [3]	23·391	0·621 or 2·604 p.c.
101. Dibenzyl	57·6	2·3853 [1]	24·713	
,, † corrected to	15·0	—	24·977	
102. Triphenylmethane	93·0	2·7700 [2]	35·527	
,, † corrected to	15·0	—	36·011	
103. Phenanthrene (solution in toluene $C_{14}H_{10} + 6C_7H_8$)	15·0	(p. 1196)	36·955	
104. Acenaphthene	99·0	3·5284 [1]	28·252	
,, corrected to‡	15·0	—	28·636	
105. Diphenyl................	93·8	2·9402 [2]	24·815	
,, † corrected to....	15·0	—	25·304	
106. Hydrindene I	14·8	2·0425	13·986	
,, II (synthetically prepared)	81·1	2·0401	13·899	
,, corrected to	15·0	—	13·928	
107. Indene I (from coal tar) ..	15·6	2·4353	15·350	
,, II (from coal tar, purified as picrate)	21·5	2·4481	15·253	
Indene III (from coal tar)	16·0	2·4357	14·946	
Average of the three samples, corrected to	15·0	—	15·200	
Indene IV (synthetical)	15·3	2·5057	16·202	
Aromatic Alcohols, Aldehydes, and Ketones.				
108. Benzylic alcohol..........	18·0	2·1672 [3]	12·406	
,, ,, corrected to	15·0	2·1700	12·400	
,, ,, ...	95·5	2·0860	12·234	0·222 or 1·78 p.c.
109. Cuminic alcohol..........	13·3	1·8707	15·883	
,, ,, corrected to	15·0	—	15·879	
110. Methylsaligenin	15·3	2·0293 [2]	14·828	
111. Anisic alcohol............	16·5	2·2345 [2]	15·404	
,, ,, corrected to	15·0	—	15·407	
112. Benzaldehyde............	11·9	2·1186 [3]	11·874	
,, corrected to	15·0	2·1153	11·864	
,, ...	94·2	1·9956	11·567	0·373 or 3·144 p.c.
113. Cuminaldehyde	14·9	1·8204	15·245	
,, ,, corrected to	15·0	—	15·245	
114. Anisaldehyde	16·8	2·3619	15·865	
,, corrected to	15·0	—	15·872	

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* From the sulphonic acid.

† By temp. diff. of diphenylmethane.

‡ By temp. diff. of naphthalene.

	T.	Specific rotation.	Molecular rotation.	Temperature difference for 100° on mol. rot.
115. Methylsalicylaldehyde	19·8	2·1231 [3]	14·169	
,, corrected to	15·0	—	14·187	
116. Salicylaldehyde	11·9	2·2674 [3]	13·298	
,, ,, corrected to	15·0	—	13·286	
117. Acetophenone............	14·2	1·9532 [2]	12·599	
,, corrected to	15·0	1·9517	12·597	
,, ...	47·4	1·9025 [1]	12·494	0·3162 or 2·510 p. c.
118. Benzophenone	54·0	2·5051 [3]	23·102	
,, corrected to	15·0	—	23·371	
,, ...	90·0	2·4633 [2]	22·854	0·689 or 2·948 p. c.
119. Ethyl phenyl ketone......	16·1	1·8574 [2]	13·632	
,, ,, corrected to	15·0	—	13·635	
120. *a*-Hydrindone	50·1	2·0473 [2]	13·657	
,, corrected to	15·0	—	13·768	
121. Coumarone........	18·5	2·4328 [2]	14·805	
,, corrected to...	15·0	—	14·807	
Halogen Derivatives and Nitriles of Aromatic Hydrocarbons.				
122. Fluorobenzene...........	19·0	1·9144	9·959	
,, corrected to*	15·0	—	9·970	
123. Chlorobenzene	17·5	2·2211 [4]	12·504	
,, corrected to	15·0	2·2268	12·510	
,, ...	84·0	2·0938 [1]	12·249	0·379
,, ...	91·5	2·0834 [1]	12·224	0·378
,, (average of the two preceding determinations)	87·3	2·0892	12·238	0·3773 or 3·046 p. c.
124. Paradichlorobenzene......	64·5	2·0857 [3]	13·487	
,, corrected to	15·0	—	13·655	
125. Bromobenzene...........	14·4	2·4937 [5]	14·503	
,, corrected to	15·0	2·4932	14·506	
,, ...	84·0	2·3548	14·191	0·455
,, ...	92·0	2·3468	14·176	0·428
,, average of the two preceding determinations	88·0	2·3504	14·182	0·4361 or 3·007 p. c.
126. Iodobenzene	10·4	3·1176 [5]	19·143	
,, corrected to ..	15·0	3·1024	19·108	
,, ...	54·9	2·9910 [3]	18·796	0·773 †
,, ...	85·1	2·9368	18·616	0·742
127. Orthochlorotoluene	15·4	2·1226 [3]	13·719	
128. Parachlorotoluene	15·2	2·0259 [3]	13·246	
129. Benzylic chloride	15·3	2·2008 [4]	14·013	
,, ,, corrected to	15·0	—	14·014	
130. Orthobromotoluene.......	16·7	2·3556 [5]	15·667	
,, ...	15·0	—	15·674	
131. Parabromotoluene........	39·0	2·2084 [3]	15·062	
,, corrected to	15·0	—	15·167	
,, ...	89·0	2·1351 [2]	14·842	0·440 or 2·901 p. c.
132. Phenylic sulphide	16·4	3·2073 [4]	29·654	
,, ,, corrected to	15·0	3·2113	29·668	
,, ,, ...	85·8	3·0653	28·963	0995 or 3·356 p. c.

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* By temp. diff. for chlorobenzene.

† Average temp. diff. for 100° = 0·756 or 3·97 per cent.

	T.	Specific rotation.	Molecular rotation.	Temperature difference for 100° on mol. rot.
133. Thiophen................	17·7	2·1867 [2]	9·555	
,, corrected to	15·0	—	9·578	
134. Benzylic sulphide	50·8	2·6002 [2]	28·864	
,, ,, corrected to*	15·0	—	29·216	
135. Thiocarbanil (phenylsenföl)	17·2	3·2606 [2]	21·515	
,, corrected to†	15·0	—	21·526	
136. Benzenesulphonic chloride.	16·6	1·9972 [2]	14·161	
,, ,, corrected to	15·0	—	14·167	
137. Benzoic chloride..........	15·7	1·9324 [2]	12·383	
,, ,, corrected to	15·0	—	12·385	
138. Phthalic chloride	15·5	1·7868 [2]	14·181	
,, ,, corrected to	15·0	—	14·183	
139. α-Toluic chloride.........	15·8	1·9280 [3]	14·088	
,, ,, corrected to	15·0	—	14·091	
140. Metachloraniline.........	14·0	2·9316 [2]	16·974	
,, corrected to	15·0	—	16·969	
,, ...	72·0	2·8153	16·662	
141. Parachloraniline	73·7	2·8287 [2]	16·751	
,, corrected to	15·0	—	17·066	
142. Benzonitrile.............	15·7	2·0918	11·854	
,, corrected to	15·0	—	11·853	
143. Paratolunitrile...........	31·1	1·9507 [2]	12·938	
,, corrected to‡	15·0	—	12·999	
144. Orthotolunitrile	15·7	1·9906 [2]	12·977	
,, corrected to	15·0	—	12·980	
145. Benzylic cyanide.........	15·2	1·9596 [2]	12·472	
,, ,, corrected to	15·0	—	12·472	
146. α-Naphthonitrile	15·1	3·2563 [2]	24·788	
147. β-Naphthonitrile.........	71·2	3·3178 [3]	25·811	
,, corrected to§	15·0	—	26·264	

Aromatic Bases.

	T.	Specific rotation.	Molecular rotation.	Temperature difference for 100° on mol. rot.
148. Aniline.................	12·4	3·2006 [2]	16·097	
,, corrected to......	15·0	3·1905	16·076	
,, ...	62·0	3·0440	15·707	0·784 } ¶
,, ...	91·0	2·9852	15·535	0·715 }
149. Methylaniline............	15·7	3·2699 [3]	19·620	
,, corrected to	15·0	—	19·624	
150. Dimethylaniline	22·6	3·2498 [2]	22·817	
,, corrected to	15·0	3·2758	22·888	
,, ...	91·3	3·0723 [3]	22·181	0·936 or 4·0876 p.c.
151. Ethylaniline	15·2	2·9498 [2]	20·567	
152. Diethylaniline...........	15·3	2·8535 [2]	25·163	
153. Methyldiphenylamine.....	17·5	3·6023 [2]	34·860	
,, ...	15·0	—	34·878	
154. Benzylamine.............	12·5	2·2719 [2]	13·664	
,, corrected to.	15·0	—	13·646	

* By temp. diff. of phenylic sulphide.

† By temp. diff. for phenylic sulphide.

‡ By temp. diff. of benzaldehyde.

§ By the estimated temp. diff. 0·453 for 100°.

¶ Average = 0·754 for 100° or 4·61 per cent.

	T.	Specific rotation.	Molecular rotation.
155. Benzylamine and water (equal volumes at 15°)	15·0	1·6389*	19·739*
„ „	15·0	1·6157†	19·154†
„ „ calculated	—	—	19·687
156. Dibenzylamine	15·6	2·4427 [3]	25·875
„ corrected to	15·0	—	25·879
157. Benzylaniline	19·5	3·2831 [2]	31·261
„ corrected to	15·0	—	31·295
158. Phenylazoimide	16·5	2·4372 [3]	14·758
„ „ corrected to	15·0	—	14·769
159. Phenylhydrazine	22·0	3·2967 [2]	18·009
„ „ corrected to	15·0	—	18·061
160. Paratoluidine	50·0	2·5979 [2]	15·871
„ (dissolved in an equal weight of orthotoluidine)	16·2	(p. 1209)	16·196
„ „ corrected to	15·0	—	16·188
„ (solution in alcohol, $C_7H_9N + 2C_2H_6O$)	15·0	(p. 1210)	15·463
161. Orthotoluidine	17·3	2·8956	17·183
„ corrected to	15·0	—	17·200
162. Metatoluidine	15·0	2·7163 [3]	16·210
163. Dimethylorthotoluidine	15·3	2·3167 [4]	18·615
„ corrected to	15·0	—	18·617
164. Dimethylparatoluidine	15·4	2·8693 [4]	22·839
„ corrected to	15·0	—	22·842
165. Orthoanisidine	17·5	3·0001 [3]	18·703
„ corrected to	15·0	--	18·722
166. Para-anisidine	68·8	2·8353 [2]	17·903
„ corrected to	15·0	—	18·306
167. α-Naphthylamine	32·6	5·2449 [3]	37·204
„ corrected to	15·0	—	37·478
„	83·0	5·0840 [2]	36·417‡
168. β-Naphthylamine (a fused mixture of equal weights of α- and β-naphthylamine)	82·3	(p. 1212)	34·650
„ corrected to§	15·0	—	35·700
169. Dimethyl-β-naphthylamine	49·4	5·1436 [3]	46·840
„ corrected to§	15·0	—	47·377
170. Dimethyl-α-naphthylamine	15·2	3·9575 [3]	35·994
171. *ac*-Tetrahydro-β-naphthylamine	15·3	2·0446 [4]	16·147
172. *ar*-Tetrahydro-α-naphthylamine	16·4	2·6172 [2]	20·048
„ „ „ corrected to	15·0	—	20·058
173. Pyridine	11·9	1·9721 [2]	8·762
„ corrected to	15·0	—	8·748
174. Quinoline	16·0	3·1958 [2]	20·861
„ corrected to	15·0	—	20·857
175. Tetrahydroquinoline	16·5	2·8169 [3]	19·613
„ corrected to	15·0	—	19·619
176. Metaphenylenediamine	15·2	3·5762 [3]	18·843
177. Orthophenylenediamine (in solution in aniline, $C_6H_4(NH_2)_2 + 1{\cdot}5C_6H_5{\cdot}NH_2$)	74·4	(p. 1214)	18·946
„ corrected to	15·0	—	19·391

* Unmixed (see pp. 1057, 1208).

† Mixed (see p. 1208).

‡ Temp. diff. for 100° on mol. rotation 1·561 or 4·165 per cent.

§ By temp. diff. of α-naphthylamine.

	T.	Specific rotation.	Molecular rotation.
178. Dimethylparaphenylenediamine	18·5	3·6051 [2]	26·213
„ corrected to	15·0	—	26·239
179. Benzamide (solution in watery phenol, $C_7H_7NO + 2(C_6H_6O + H_2O)$)	15·25	(p. 1216)	13·520
180. Formanilide	14·3	2·5979 [2]	15·214
„ corrected to	15·0	—	15·211
„	61·7	2·5141 [2]	14·961*
181. Acetanilide (in solution in phenol, $C_8H_9NO + 1{\cdot}5C_6H_6O$)	71·4	(p. 1216)	15·702
„ corrected to†	15·0	—	16·003
182. Phenylacetamide (in solution in phenol, $C_8H_9NO + 2{\cdot}5C_6H_6O$)	78·5	(p. 1217)	14·869
„ corrected to†	15·0	—	15·208
Hydrochlorides of Bases.			
183. Aniline hydrochloride (in aqueous solution, $C_6H_7N,HCl + 9{\cdot}722H_2O$)	14·2	(p. 1218)	15·547
„ „ „ ‡	—	—	16·394
184. Dimethylaniline hydrochloride (anhydrous)	16·7	(p. 1218)	18·326
Dimethylaniline hydrochloride (anyhydrous) (I. In aqueous solution, $C_8H_{11}N,HCl + 0{\cdot}069HCl + 6{\cdot}174H_2O$)	13·8	(p. 1220)	17·606
(II. In aqueous solution, $C_8H_{11}N,HCl + 0{\cdot}069HCl + 21{\cdot}238H_2O$)	14·8	(p. 1221)	17·351
185. Hydrochlorides of dimethylparatoluidine (in aqueous solution, $C_9H_{13}N,HCl + 0{\cdot}5HCl + 4{\cdot}17H_2O$)	18·0	(p. 1221)	18·465
Hydrochlorides of dimethylorthotoluidine (in aqueous solution, $C_9H_{13}N,HCl + 0{\cdot}5HCl + 4{\cdot}17H_2O$)	17·0	(p. 1222)	18·705
186. Hydrochloride of orthophenylenediamine (in aqueous solution, $C_6H_8N_2,2HCl + 45H_2O$)	15·0	(p. 1222)	21·329
Hydrochloride of paraphenylenediamine (in aqueous solution, $C_6H_8N_2,2HCl + 65H_2O$)	15·0	(p. 1223)	20·213
Hydrochloride of metaphenylenediamine (in aqueous solution, $C_6H_8N_2,2HCl + 40H_2O$)	15·0	(p. 1223)	20·345
Unsaturated Compounds.			
187. Cinnamene	18·73	2·5527 [3]	16·015
„ corrected to	15·0	—	16·041
188. Allylbenzene	18·2	2·4458 [2]	17·578
„ corrected to	15·0	—	17·599
189. Isobutenylbenzene	19·3	2·2628 [3]	18·333
„ corrected to	15·0	—	18·362
190. Stilbene (a solution in diphenylmethane containing 26·315 per cent. of stilbene)	69·6	(p. 1225)	32·666
„ §corrected to	15·0	—	33·143

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* Temp. diff. for 100° on mol. rotation, 0·534.

† By temp. diff. of formanilide.

‡ Estimated as dry aniline hydrochloride, being corrected for the influence of solution by the results obtained with dimethylaniline.

§ Estimated temp. diff. for 54·6° = 0·477.

	T.	Specific rotation.	Molecular rotation.
191. Phenyl allyl oxide	14·1	2·2694 [2]	17·141
,, ,, ,, corrected to	15·0	2·2672	17·134
,, ,, ,,	86·4	2·1217 [4]	16·647*
192. Paratolyl allyl oxide	15·7	2·0775 [3]	17·566
,, ,, ,, corrected to	15·0	—	17·571
193. Anethole	16·1	2·5459 [4]	21·082
,, corrected to	15·0	—	21·089
194. Allylic benzoate	15·2	1·8458 [2]	15·722
195. Isoeugenol	19·3	2·5578 [2]	21·445
,, corrected to	15·0	—	21·469
196. Eugenol	15·4	2·1974 [3]	18·724
,, corrected to	15·0	—	18·727
197. Cinnamaldehyde	15·7	2·7126 [3]	17·880
,, ,, corrected to	15·0	—	17·885
198. Ethylic cinnamate	16·3	2·1551 [3]	19·998
,, ,, corrected to	15·0	2·1577	20·006
,, ,,	92·3	2·0394 [1]	19·477†
199. α-Methylic orthomethoxyphenylacrylate	15·5	2·3397 [3]	21·888
,, ,, ,, corrected to	15·0	—	21·891
200. β-Methylic orthomethoxyphenylacrylate	15·4	2·3954 [3]	22·356
,, ,, ,, corrected to	15·0	—	22·359
201. Cinnamic alcohol	37·1	2·4854 [2]	17·808
,, ,, corrected to	15·0	—	17·940
,, ,,	89·3	2·4116 [2]	17·494‡
202. Benzylidene-acetone	17·0	2·4560 [2]	19·221
,, ,, corrected to	15·0	—	19·235

BOILING POINTS.

Alcohols.

Substance.	Perkin.	Other observers.
Anisic alcohol	216° (250 mm.)	258·8°, Cannizzaro.
Benzylic alcohol	205·3° (corr.)	204·7, Kahlbaum.
Benzyl methyl oxide	170·5 ,,	167·5, Cahours.
Cinnamic alcohol	257·5 ,,	254·0 (747·3 mm.), Brühl.
Cuminic alcohol	248·7 ,,	246·6 (corr.), Kraut.
Methylsalicylic alcohol	179·5 (250 mm.)	247·5 (765 mm.), Cannizzaro-Körner.

Aldehydes.

Substance.	Perkin.	Other observers.
Anisaldehyde	248·0° (corr.)	247·5° (733·5 mm.), Rossel.
Benzaldehyde	178·7 ,,	180·0, Kahlbaum.
Cinnamaldehyde	209·5 (250 mm.).	
Cuminaldehyde	235·5 (corr.)	237·0, Kopp.
Methylsalicylaldehyde	243·0 ,,	238·0, Voswinckel.
Salicylaldehyde	197·0 ,,	196·5, Piria.

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* Temp. diff. for 100° on mol. rotation, 0·719 or 4·196 per cent.

† Temp. diff. for 100° on mol. rotation, 0·685 or 3·425 per cent.

‡ Temp. diff. for 100° on mol. rotation, 0·6015 or 3·352 per cent.

Amides.

Substance.	Perkin.	Other Observers.
Acetanilide.........	305·0° (corr.)	301·5° (725 mm.), Pictet-Crépieux.
Phenylacetamide ...	262·0 (250 mm.).	

Amines.

Aniline	184·0° (corr.)	183·7°, Thorpe.
o-Anisidine..	225·0 ,,	226·5 (734 mm.), Mühlhäuser.
p-Anisidine.........	243·0 ,,	245·5, Salkowski.
Benzylamine........	184·5 ,,	185·0, Rudolph.
Dibenzylamine......	269·0 (250 mm.).	
Diethylaniline	216·2 ,,	216·5 (769·5 mm.), R. Schiff.
Dimethylaniline	193·0 ,,	192·6 (738·4 mm.), Brühl.
Dimethyl-*α*-naphthylamine............	184·5 (69 mm.).	
Dimethyl-*β*-naphthylamine............	212·5 (69 mm.).	
Dimethyl-*p*-phenylenediamine	262·3 (corr.)	257·0, Wurster.
Dimethyl-*o*-toluidine	185·5 ,,	183·0, Wurster-Roser.
Dimethyl-*p*-toluidine	211·2 ,,	208·0, Hofmann.
Ethylaniline	205·5 ,,	206·0, Pictet-Crépieux.
Methylaniline	195·5 ,,	193·5 (760 mm.), Pictet-Crépieux.
Methyldiphenylamine	296·0 ,,	292·0 (740·8 mm.), Brühl.
α-Naphthylamine....	300·8 ,,	300·0, Zinin.
β-Naphthylamine ...	306·1 ,,	294·0, Liebermann-Jacobson.
m-Phenylenediamine.	283·0 ,,	276·5, Zincke-Sintenis.
o-Phenylenediamine .	257·0 ,,	252·0, Griess.
Phenylhydrazine	243·5 ,,	241·5 (750 mm.), E. Fisher.
Pyridine	116·4 ,,	116·1 (759·5 mm.), R. Schiff.
Quinoline	238·0 ,,	238·0, Kahlbaum.
Tetrahydro-*α*-naphthylamine, *ac*-	210·0 (250 mm.).	
Tetrahydro-*β*-naphthylamine, *ar*-	234·0 (250 mm.).	
Tetrahydroquinoline .	251 0 (corr.)	244·0, Wischnegradsky.
o-Toluidine.........	199·5 ,,	198·4 (735·4 mm.), Brühl.
p-Toluidine.........	200·3 ,,	198·0, Muspratt-Hofmann.
m-Toluidine	203·0 ,,	

Halogen Compounds.

Benzenesulphonic chloride	251 5° (corr.)	246·5, Otto.
Benzoic chloride	197·2 ,,	194·0 (742·2 mm.), Brühl.
Benzylic chloride	179·0 ,,	179·0°, Kahlbaum.
Bromobenzene	155·0 ,,	155·6, Schiff.
o-Bromotoluene	181·0 ,,	182·2 (761·8 mm.), R. Schiff.
p-Bromotoluene.....	183·8 ,,	185·2, Hübner-Post.
m-Chloraniline	236·5 ,,	230·0 (767·3 mm.) Beilstein-Kurbatow.
p-Chloraniline	232·3 ,,	230·5, Mills.
Chlorobenzene......	131·5 ,,	132·0, R. Schiff.

Substance.	Perkin.	Other Observers.
o-Chlorotoluene	159·1° (corr.)	159·38° (corr.), Feitler.
p-Chlorotoluene	162·0 ,,	161·5, Kahlbaum.
p-Dichlorobenzene	173·7 ,,	173·2, Körner.
Fluorobenzene	—	85·0, Sydney Young.
Iodobenzene	187·7 (corr.)	187·7, R. Schiff.
Phthalic chloride	281·1 ,,	275·4 (726 mm.), Brühl.
a-Toluic chloride	170·0 (250 mm.)	102·5 (17 mm.), Anschütz-Berns.

Hydrocarbons.

Substance.	Perkin.	Other Observers.
Acenaphthene	229·5° (250 mm).	277·5°, Behr.
Allylbenzene	176·5 (corr.)	
Benzene	80·3 ,,	80·36, Regnault.
iso-Butenylbenzene	187·8 ,,	181·0, Liebmann.
iso-Butylbenzene	169·2 ,,	167·5, Radziszewsky.
Cymene (from sulphonic acid)	177·3 ,,	
Dibenzyl	281·5 ,,	284·0, Cannizzaro-Rossi.
Diphenylmethane	264·7 ,,	261·5, Zincke.
Ethylbenzene (from sulphonic acid)	135·5 ,,	135·8 (758·5 mm.), R. Schiff.
Hydrindene (coal-tar)	176·25 ,,	176·2, Krämer-Spilker.
,, (synthetical)	177·0 ,,	
Indene (coal-tar)	180·0 ,,	180·0 (corr.), Krämer-Spilker.
Indene (synthetical).	181·0 ,,	
Mesitylene	164·1 ,,	164·5 (759·2 mm.), R. Schiff.
Naphthalene	218·0 ,,	218·1, Crofts.
Propylbenzene	159·2 ,,	158·5, R. Schiff.
iso-Propylbenzene (cumene)	152·9 ,,	152·75, Liebmann.
Pseudocumene	168·2 ,,	169·8 (corr.), Warren.
Toluene (from sulphonic acid)	110·6 ,,	110·3, Neubeck.
Triphenylmethane	306·0 (250 mm.)	359·5 (754 mm.), Crofts.
m-Xylene	139·3 (corr.)	139·2 (759·2 mm.), R. Schiff.
o-Xylene	142·6 ,,	142·5, Jacobson.
p-Xylene	137·5 ,,	138·0, R. Schiff.

Ketones.

Substance.	Perkin.	Other Observers.
Acetophenone	202·0° (corr.)	202·0°, Fittig.
Benzophenone	306·1 ,,	306·0, Croft.
Ethyl phenyl ketone.	142·3 (78 mm.)	218·0, Morley-Green.
Coumarone	174·0 (corr.)	

Nitriles.

Substance.	Perkin.	Other Observers.
a-Naphthyl cyanide .	299·0° (corr.)	297·5° (corr.), Merz-Mühlhäuser.
β-Naphthyl cyanide .	306·5 ,,	304·5 ,, Merz-Mühlhäuser.
Benzonitrile	190·7 ,,	190·7 ,, Kopp.
Benzylic cyanide	233·5 ,,	231·7 ,, Hofmann.
o-Tolunitrile	2 5·2 ,,	203·5 ,, Weith.
p-Tolunitrile	217·6 ,,	217·8, Paternò.

Nitro-compounds.

Substance.	Perkin.	Other Observers.
Nitrobenzene	210·8° (corr.)	209·4° (745·4 mm.), Brühl.
o-Nitrotoluene	225·7 ,,	223·0, Kekulé.

Phenols and Derivatives.

Anethole	235·3° (corr.)	
Carvacrol	237·7 ,,	236·7°, Jacobson.
Creosol	—	130·5 (50 mm.), W. H. Perkin, Jun.
iso-Creosol	181·0 (250 mm.).	
m-Cresol	202·0 (corr.)	202·8, Pinette.
o-Cresol............	191·0 ,,	188·0, Berthelot.
p-Cresol............	198·0 ,,	201·8, Pinette.
Dimethylguaiacol (veratrole)	207·2 ,,	205·5, Marasse.
Dimethylhomopyrocatechol	220·5 ,,	218·0, Goldschmidt.
Dimethylquinol.....	212·6 ,,	
Dimethylresorcinol ..	216·7 ,,	214·5 (759 mm.), R. Schiff.
Eugenol	253·5 ,,	247·5, Wassermann.
iso-Eugenol	193·5 (100 mm.).	
Guaiacol...........	205·0 (corr.)	205·1, Béhal-Choay.
Homopyrocatechol ..	—	251·5, W. H. Perkin, Jun.
α-Naphthylethyloxide	279·8 (corr.)	280·7 (corr.), Schäffer.
β-Naphthylethyloxide	282·0 ,,	274·5, Liebermann-Hagen.
Phenol.............	182·6 ,,	182·3 (corr.), Ladenburg.
Phenyl allyl oxide ..	191·7 ,,	192—195, Henry.
Phenyl ethyl oxide..	170·3 ,,	170·3, Pinette.
Phenyl *iso*-butyl oxide	199·9 ,,	198·0, Riess.
Phenyl methyl oxide.	153·9 ,,	154·3, Pinette.
Phenyl octyl oxide ..	285·2 ,,	
Phenyl propyl oxide.	189·3 ,,	190·5, Pinette.
Phenyl *iso*-propyloxide	177·2 ,,	176·0, Silva.
Pyrogallol..........	309·0 ,,	293·0 (730 mm.), J. Schmidt.
Thymol............	233·5 ,,	230·0, Lallemand.
p-Tolyl allyl oxide ..	214·5 ,,	
m-Tolyl methyl oxide	176·7 ,,	177·2, Pinette.
o-Tolyl methyl oxide.	171·1 ,,	171·3, Pinette.
p-Tolyl methyl oxide.	176·5 ,,	175·5 (762·3 mm.), R. Schiff.
Trimethylpyrogallol..	241·0 ,,	235·0 (corr.), Will.

Salts.—Ethereal Salts.

Allylic benzoate.....	230·0° (corr.)	230·0°, Berthelot-Luca.
Butylic benzoate	249·0 ,,	247·3 (corr.), Linnemann.
iso-Butylic benzoate .	241·5 ,,	237·0 ,, Kahlbaum.
Ethylic anisate......	269·5 ,,	252·5, Cahours.
Ethylic benzoate	211·8 ,,	211·2 (corr.), R. Schiff.
Ethylic cinnamate...	226·0 (250 mm.).	
Ethylic cuminate....	263·6 (corr.)	240·0 (Gerhardt and Cahours).

Substance.	Perkin.	Other Observers.
Ethylic hydrocinnamate	247·2° (corr.)	247·5° (corr.), Erlenmeyer.
Ethylic *m*-methoxybenzoate	252·0 „	
Ethylic methylsalicylate	261·5 „	235·0 „ Fölsing.
Ethylic α-naphthoate	220·5 (74 mm.).	
Ethylic β-naphthoate	224·0 (74 mm.).	
Ethylic phenylacetate	227·3 (corr.)	229·0 „ Hodgkinson.
Ethylic phthalate	298·5 „	
Ethylic *iso*-phthalate	302·0 „	285·0, Fittig-Storrs.
Ethylic terephthalate	302·0 „	
Ethylic salicylate	233·7 „	231·5 (corr.), Kahlbaum.
Ethylic *o*-toluate	227·0 „	219·5 (713 mm.), Ador-Rillict.
Ethylic *p*-toluate	235·5 „	228·0, Noad.
Methylic benzoate	198·6 „	199·2 (746 mm.), Kopp.
Methylic α-*o*-methoxyphenylacrylate	301·5 „	
Methylic β-*o*-methoxyphenylacrylate	304·5 „	
Methylic salicylate	222·2 „	224·0 (corr.), Kopp.
Octylic benzoate	259·4 (210 mm.)	305·5, Zincke.
Propylic benzoate	230·7 (corr.)	229·5 (corr.), Linnemann.
iso-Propylic benzoate	218·5 „	218·0, Linnemann.

Salts.—Phenylic Salts.

Phenylic acetate	196·7° (corr.).	193·0°, Hodgkinson and Perkin, Jun.
Phenylic butyrate	227·5 „	
Phenylic œnanthate	282·3 „	277·5, Cahours.
Phenylic propionate	211·0 „	200·0 (744 mm.), Prevost.

Sulphur Compounds.

Phenylic sulphide	296·5° (corr.)	293·0°, Kraft-Lyons.
Thiocarbanil	221·0 „	219·8 (768·8 mm.), R. Schiff.
Thiophen	84·0 „	84·0, Schiff.

INDEX.

Compounds of the Fatty Series.

Substance.	Mol. rot. 15°.	Page
Acetic acid	2·528	1063, *1172*, *1236*.*
Chloracetic acid	3·882	1063, *1172*, *1236*.
Citraconic anhydride	5·543	1063, *1173*, *1237*.
Dichloracetic acid	5·300	1063, *1172*, *1236*.

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* The numbers in *italics* refer to the experimental results, p. 1169 *et seq.*

Substance.	Mol. rot. 15°.	Page
Dimethylacetylacetone	7·045	1063, *1172*, *1237*.
Dipropyl ketone	7·471	1063, *1172*, *1236*.
Ethylene dichloride	5·484	1063, *1173*, *1237*.
Ethylic acetoacetate	6·502	1063, *1172*, *1236*.
Ethylic citraconate	10·497	1063, *1173*, *1237*.
Ethylic iodide	10·082	1063, *1173*, *1237*.
Ethylic œnanthate	9·542	1063, *1172*, *1236*.
Heptane	7·666	1063, *1172*, *1236*.
Hydracetylacetone	5·871	1063, *1172*, *1237*.
Methylene diiodide	18·644	1063, *1173*, *1237*.
Octylic bromide	12·025	1063, *1173*, *1236*.
Octylic chloride	10·139	1063, *1173*, *1237*.
Octylic iodide	16·182	1063, *1173*, *1237*.
Œnanthylic acid	7·554	1063, *1172*, *1236*.
Propionic acid	3·464	1063, *1172*, *1236*.
Propylic bromide	6·880	1063, *1173*, *1237*.
Pyrotartaric anhydride	4·759	1063, *1173*, *1237*.
Trichloracetic acid	6·473	1063, *1172*, *1236*.
Aromatic Compounds: Acids.		
Phenylacetic acid	12·743	1079, 1094, *1175*, *1238*.
Alcohols and Ethers.		
Anisic alcohol	15·407	1128, 1136, *1199*, *1242*.
Benzylic alcohol	12·400	1064, 1090, 1125, *1198*, *1242*.
Benzyl methyl oxide	13·417	1090, *1190*, *1241*.
Cinnamic alcohol	17·940	1064, 1126, 1149, *1228*, *1247*.
Cuminic alcohol	15·879	1125, *1198*, *1242*.
Methylsalicylic alcohol	14·828	1128, *1198*, *1242*.
Aldehydes.		
Anisaldehyde	15·872	1128, 1136, *1200*, *1242*.
Benzaldehyde	11·864	1064, 1091, 1125, *1199*, *1242*.
Cinnamaldehyde	17·885	1126, 1145, 1149, *1227*, *1247*.
Cuminaldehyde	15·245	1125, *1199*, *1242*.
Methylsalicylaldehyde	14·187	1127, 1128, *1200*, *1243*.
Salicylaldehyde	13·286	1126, *1200*, *1243*.
Amides.		
Acetanilide	16·003	1114, *1216*, *1246*.
Benzamide	13·520	1114, *1216*, *1246*.
Formanilide	15·211	1114, *1216*, *1246*.
Phenylacetamide	15·208	1114, *1217*, *1246*.
Amines.		
Aniline	16·076	1064, 1098, 1155, *1207*, *1244*.
o-Anisidine	18·722	1131, *1211*, *1245*.
p-Anisidine	18·306	1131, *1211*, *1245*.
Benzylamine	13·646	1103, 1157, *1208*, *1245*.
Benzylaniline	31·295	1102, *1209*, *1232*, *1245*.

Substance.	Mol. rot. 15°.	Page.
m-Chloraniline	16·969	1131, *1205*, *1244*.
p-Chloraniline	17·066	1131, *1205*, *1244*.
Dibenzylamine	25·879	1103, *1208*, *1245*.
Diethylaniline	25·163	1099, 1100, *1208*, *1244*.
Dimethylaniline	22·888	1064, 1099, 1100, 1108, 1156, *1207*, *1232*, *1244*.
Dimethyl-α-naphthylamine	35·994	1108, 1138, 1156, *1213*, *1233*, *1245*.
Dimethyl-β-naphthylamine	47·377	1108, 1138, 1156, *1212*, *1234*, *1245*.
Dimethyl-*p*-phenylenediamine	26·239	1109, *1215*, *1246*.
Dimethyl-*o*-toluidine	18·617	1108, 1138, 1156, *1211*, *1233*, *1245*.
Dimethyl-*p*-toluidine	22·842	1108, 1138, 1156, *1211*, *1233*, *1245*.
Ethylaniline	20·567	1099, *1208*, *1244*.
Methylaniline	19·624	1099, *1207*, *1244*.
Methyldiphenylamine	34·878	1101, 1157, *1208*, *1232*, *1244*.
α-Naphthylamine	37·478	1064, 1107, 1134, 1155, 1160, *1211*, *1245*.
β-Naphthylamine	35·700	1107, 1134, 1155, 1160, *1212*, *1233*, *1245*.
m-Phenylenediamine	18·843	1109, 1131, 1155, *1214*, *1232*, *1245*.
o-Phenylenediamine	19·391	1104, 1109, 1131, *1214*, *1245*.
Phenylhydrazine	18·061	1104, *1209*, *1245*.
Pyridine	8·748	1115, *1214*, *1245*.
Quinoline	20·875	1115, 1117, *1214*, *1245*.
Tetrahydro-α-naphthylamine *ar*	20·058	1104, 1106, *1213*, *1245*.
Tetrahydro-β-naphthylamine *ac*	16·147	1104, 1106, *1213*, *1245*.
Tetrahydroquinoline	19·619	1117, *1214*, *1245*.
m-Toluidine	16·210	1131, *1210*, *1245*.
o-Toluidine	17·200	1104, 1131, 1155, 1159, *1210*, *1245*.
p-Toluidine	16·188	1131, 1155, 1159, *1209*, *1245*.

Amine Hydrochlorides.

Substance.	Mol. rot. 15°.	Page.
Aniline (dry)	16·394	1111, 1159, *1218*.
,, (in sol.)	15·547	1111, 1159, *1218*, *1235*, *1246*.
Dimethylaniline (dry)	18·326	1110, 1158, *1218*, *1235*, *1246*.
,, (sol. strong)	17·604	1110, 1158, *1220*, *1235*, *1246*.
,, (sol. weak)	17·351	1110, *1221*, *1246*.
o-Dimethyltoluidine (in sol.)	18·705	1111, 1131, 1139, *1222*, *1246*.
p-Dimethyltoluidine (in sol.)	18·465	1111, 1131, 1139, *1221*, *1246*.
m-Phenylenediamine (in sol.)	20·345	1112, 1132, *1223*, *1246*.
o-Phenylenediamine (in sol.)	21·329	1112, 1132, *1222*, *1246*.
p-Phenylenediamine (in sol.)	20·213	1112, 1132, *1223*, *1246*.

Azoimide.

Substance.	Mol. rot. 15°.	Page.
Phenylazoimide	14·769	1098, 1154, *1209*, *1232*, *1245*.

Haloid Compounds.

Substance.	Mol. rot. 15°.	Page.
Benzenesulphonic chloride	14·167	1123, *1205*, *1244*.
Benzoic chloride	12·385	1121, *1205*, *1244*.
Benzylic chloride	14·014	1120, *1203*, *1243*.
Bromobenzene	14·506	1064, 1118, 1119, *1202*, *1243*.
o-Bromotoluene	15·674	1131, *1203*, *1243*.
p-Bromotoluene	15·167	1064, 1131, *1204*, *1243*.
m-Chloraniline	16·969	1106, *1205*, *1244*.
p-Chloraniline	17·066	1106, *1205*, *1244*.
Chlorobenzene	12·510	1064, 1118, 1119, *1202*, *1243*.
o-Chlorotoluene	13·719	1131, *1203*, *1243*.
p-Chlorotoluene	13·246	1131, *1203*, *1243*.
p-Dichlorobenzene	13·655	1120, *1202*, *1243*.
Fluorobenzene	9·970	1118, 1119, 1162, *1201*, *1243*.
Iodobenzene	19·108	1064, 1118, 1119, *1203*, *1243*.
Phthalic chloride	14·183	*1205*, *1244*.
a-Toluic chloride	14·091	1122, *1205*, *1244*.

Hydrocarbons.

Substance.	Mol. rot. 15°.	Page.
Acenaphthene	28·636	1088, 1089, *1196*, *1242*.
Allylbenzene	17·599	1084, 1126, 1143, 1149, *1224*, *1246*.
Benzene	11·284	1064, 1082, 1084, 1085, *1191*, *1241*.
iso-Butenylbenzene	18·362	1143, *1224*, *1229*, *1246*.
iso-Butylbenzene	15·615	1082, 1083, *1192*, *1241*.
Cinnamene	16·041	1143, 1149, *1224*, *1246*.
Cymene (methylisopropylbenzene)	15·255	1125, *1194*, *1242*.
Dibenzyl	24·977	1085, 1086, *1195*, *1242*.
Diphenyl	25·304	1085, 1087, 1089, 1153, *1196*, *1230*, *1242*.
Diphenylmethane	23·845	1064, 1085, 1086, 1152, *1195*, *1230*, *1242*.
Ethylbenzene	13·414	1079, 1082, 1083, 1094, 1096, *1192*, *1241*.
Hydrindene (coal tar)	13·985	*1196*, *1229*, *1242*.
,, (synthetical)	13·928	1083, 1144, 1153, *1197*, *1242*.
Indene (coal tar average)	15·200	*1196*, *1230*, *1242*.
,, (synthetical)	16·202	1083, 1144, 1153, *1197*, *1230*, *1242*.
Mesitylene	13·366	1064, 1130, *1193*, *1241*.
Naphthalene	25·125	1064, 1088, 1089, *1195*, *1242*.
Phenanthrene	36·959	1088, 1151, *1196*, *1242*.
Propylbenzene	14·553	1082, 1083, 1094, *1192*, *1241*.
iso-Propylbenzene (cumene)	14·633	1082, 1083, 1084, *1194*, *1241*.
Pseudocumene	13·998	1064, 1130, *1193*, *1241*.
Stilbene	33·143	1150, *1225*, *1246*.
Toluene	12·157	1064, 1082, 1083, 1085, 1125, *1191*, *1241*.

Substance.	Mol. rot. 15°.	Page.
Triphenylmethane	36·011	1085, 1086, 1152, *1195*, *1230*, *1242*.
m-xylene	12·859	1130, 1159, *1192*, *1229*, *1241*.
o-xylene	13·345	1130, 1159, *1192*, *1229*, *1241*.
p-xylene	12·810	1130, 1159, *1193*, *1229*, *1241*.
Ketones.		
Acetophenone	12·597	1064, 1091, 1092, *1200*, *1243*.
Benzophenone	23·371	1064, 1091, 1093, *1201*, *1243*.
Benzylidene-acetone	19·235	1145, *1229*, *1247*.
Coumarone	14·807	*1201*, *1243*.
Hydrindone	13·768	1093, *1201*, *1243*.
Phenyl ethyl ketone	13·635	1091, 1093, *1201*, *1243*.
Nitriles.		
Benzonitrile	11·857	1096, *1206*, *1244*.
Benzylic cyanide	12·472	1097, *1206*, *1244*.
a-Naphthonitrile	24·788	1097, 1137, *1206*, *1244*.
β-Naphthonitrile	26·264	1137, *1206*, *1244*.
o-Tolunitrile	12·980	1096, 1137, *1206*, *1244*.
p-Tolunitrile	12·999	1137, *1206*, *1244*.
Nitro-compounds.		
m-Dinitrobenzene	9·647	1095, *1181*, *1239*.
Nitrobenzene	9·361	1064, 1094, *1180*, *1239*.
o-Nitrotoluene	10·806	1095, 1131, 1162, *1181*, *1239*.
p-Nitrotoluene	10·214	1095, 1131, *1181*, *1239*.
a-Nitronaphthalene	20·840	1096, *1181*, *1239*.
Phenols and Derivatives.		
Anethole	21·089	1148, *1226*, *1247*.
Carvacrol	16·313	1132, *1183*, *1239*.
Creosol	15·405	1127, 1135, *1185*, *1240*.
iso-Creosol	15·021	1127, *1185*, *1240*.
m-Cresol	12·776	1129, *1183*, *1239*.
o-Cresol	13·382	1126, 1129, *1182*, *1239*.
p-Cresol	12·869	1129, *1182*, *1239*.
o-Dimethoxybenzene (veratrole)	16·837	1127, 1135, 1159, *1188*, *1240*.
Dimethylhomopyrocatechol	17·484	1127, 1135, *1188*, *1240*.
Dimethylquinol	16·717	1064, 1136, *1188*, *1240*.
Dimethylresorcinol	15·108	1127, 1159, *1187*, *1240*.
Eugenol	18·727	1142, *1127*, *1247*.
iso-Eugenol	21·469	1147, *1127*, *1247*.
Guaiacol	14·689	1127, 1135, *1188*, *1240*.
Homopyrocatechol	13·306	1135, *1183*, *1239*.
a-Naphthyl ethyl oxide	32·237	1064, 1134, 1160, *1189*, *1231*, *1241*.
β-Naphthyl ethyl oxide	30·698	1134, 1160, *1190*, *1231*, *1241*.
Phenol	12·140	1064, 1090, *1181*, *1239*.
Phenyl allyl oxide	17·134	1064, 1141, *1225*, *1247*.

Substance.	Mol. rot. 15°.	Page.
Phenyl *iso*-butyl oxide	17·332	1080, 1081, *1186*, *1240*.
Phenyl ethyl oxide	15·129	1080, 1081, *1186*, *1240*.
Phenyl methyl oxide	13·958	1080, 1081, 1090, 1127, *1186*, *1240*.
Phenyl octyl oxide	21·446	1080, 1081, *1186*, *1240*.
Phenyl propyl oxide	16·187	1080, 1081, *1186*, *1240*.
Phenyl *iso*-propyl oxide	16·201	1080, 1081, *1186*, *1240*.
Pyrocatechol	13·022	1127, 1130, 1135, *1184*, *1240*.
Pyrogallol	13·029	1127, *1185*, *1240*.
Resorcinol	12·285	1127, 1130, *1084*, *1239*.
Thymol	16·120	1064, 1132, *1183*, *1239*.
p-Tolyl allyl oxide	17·571	1141, *1226*, *1247*.
m-Tolyl methyl oxide	14·646	1127, 1130, 1159, *1187*, *1240*.
o-Tolyl methyl oxide	15·190	1127, 1128, 1130, 1159, *1187*, *1240*.
p-Tolyl methyl oxide	14·712	1127, 1128, 1130, 1159, *1187*, *1240*.
Trimethylpyrogallol	17·201	1064, 1127, *1189*, *1241*.
Salts: Ethereal Salts of Aromatic Acids.		
Allylic benzoate	15·722	1141, *1226*, *1247*.
Butylic benzoate	15·952	1073, 1074, 1078, *1174*, *1238*.
iso-Butylic benzoate	16·048	1073, 1074, *1175*, *1238*.
Ethylic anisate	17·285	1128, 1136, 1160, *1176*, *1231*, *1238*.
Ethylic benzoate	13·854	1073, 1074, 1077, 1078, 1094, 1125, *1174*, *1237*.
Ethylic benzoylacetate	16·411	1064, *1178*, *1238*.
Ethylic cuminate	17·093	1125, *1176*, *1238*.
Ethylic cinnamate	20·006	1145, 1149, *1228*, *1247*.
Ethylic hydrocinnamate	16·169	1064, 1077, 1078, *1175*, *1238*.
Ethylic *m*-methoxybenzoate	16·679	1130, *1176*, *1238*.
Ethylic methylsalicylate	17·156	1127, 1128, 1230, 1160, *1176*, *1231*, *1238*.
Ethylic α-naphthoate	27·161	1137, 1161, *1179*, *1231*, *1238*,
,, β-naphthoate	27·360	1137, 1161, *1179*, *1232*, *1238*.
,, phenylacetate	14·982	1077, *1175*, *1238*.
,, phthalate	16·909	1064, 1132, *1177*, *1238*.
,, isophthalate	16·942	1132, *1177*, *1238*.
,, terephthalate	16·117	1132, *1178*, *1238*.
,, salicylate	15·366	1126, 1127, *1176*, *1238*.
Ethylic *o*-toluate	15·065	1096, 1097, 1130, *1177*, *1238*.
Ethylic *p*-toluate	14·744	1130, *1177*, *1238*.
Methylic benzoate	12·743	1073, 1074, 1094, *1173*, *1237*.
,, α-*o*-methoxyacrylate	21·891	1147, *1228*, *1247*.
,, β-*o*-methoxyacrylate	22·359	1147, *1228*, *1247*.
,, salicylate	14·266	*1176*, *1238*.
Octylic benzoate	19·992	1073, 1074, *1175*, *1238*.
Propylic benzoate	14·873	1073, 1074, *1174*, *1237*.
iso-Propylic benzoate	14·950	1073, 1074, 1078, *1174*, *1237*.

Salts: Phenylic Salts of Fatty Acids.

Substance.	Mol. rot. 15°.	Page.
Phenylic acetate	12·953	1064, 1075, 1076, *1179*, *1238*.
,, butyrate	14·761	1075, 1076, 1078, *1180*, *1238*.
,, œnanthate	17·923	1064, 1075, 1076, 1078, *1180*, *1239*.
,, propionate	13·673	1075, 1076, 1078, *1179*, *1238*.

Sulphur Compounds.

Substance.	Mol. rot. 15°.	Page.
Benzylic sulphide	29·216	1124, *1204*, *1244*.
Carbon bisulphide	10·751	1123.
Phenylic sulphide	29·668	1064, 1124, *1204*, *1243*.
Thiocarbanil	21·526	1124, *1204*, *1244*.
Thiophen	9·578	1117, *1204*, *1244*.

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